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RUBBER CHEMISTRY AND TECHNOLOGY

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EFFECT OF STRETCHING ON THE PROPERTIES OF RUBBER*

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INTRODUCTION

The most popular physical test on vulcanized rubbers has hitherto been the tensile stress-strain test. The wealth of experience and data from numerous investigations make it of importance in determining the quality of a particular rubber and enable it to be used to assess the optimum period of vulcanization or the effect of age or service. Many workers have suggested that the value of the test has been considerably overrated, as rubber articles in service seldom operate under the large strains employed in the tensile test; often they operate under small repeated deformations, and under these conditions the behavior of the rubber shows little correlation with the results of normal tensile tests. As a result, recent developments in the physical testing of rubber vulcanizates have been in the measurement of the resistance of the rubber to abrasion, tearing, flexing, and fatigue caused by repeated stressing. Although these criticisms are substantially true, it would be a mistake to neglect or underestimate the value which results from the wide experience in the use of tensile tests.

Apart from the various conclusions, already described, which can be drawn from the results of a tensile test, it shows the ultimate strength and extensibility of a rubber when it is stretched slowly, it also gives information on the modulus of the rubber and its change with extension. It is possible to relate these properties with other physical properties such as the resistance to abrasion, tearing, and flex-cracking, and recently Buist and Davies[1] have published a paper evaluating the degree of correlation between a number of such physical properties. In rubber technology the value of the load in lbs. per sq. inch of the original cross-sectional area required to give an elongation is referred to as the modulus at that elongation. This definition does not coincide with the classical definition of the term modulus, and throughout this report the terms stress or tensile-stress are used.

It has long been realized that the shape of the stress-strain curve is not reproducible, but changes with each successive deformation of the rubber test-piece; however, the normal tensile stress-strain test involves only the first extension, despite the fact that once it has been used in service the rubber will probably never return completely to the unique initial state indicated by this test. There have been numerous attempts to represent the shape of the stress-strain curve recorded during the first extension by various expressions; no particular significance could be attached to the parameters employed in the earlier empirical relations, but more recntly the kinetic theory of high-elasticity has had considerable success in accounting for the main elastic properties of rubber and in forecasting the general shape of the stress-strain curves of

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vulcanizates of so-called pure mixings, which may contain accelerators. Although the basic ideas and assumptions of this kinetic theory are now well established, it will be useful to mention them here.

Materials which show rubberlike properties are assumed to be loose networks of long-chain molecules, which are in constant thermal agitation, and as a result are randomly arranged. When the material is deformed, the molecular chains are rearranged and leave their random (more probable) configuration to take up more ordered (less probable) positions; this change can be expressed as a decrease in entropy resulting from the deformation. The forces which tend to make the rubber return to its original state are forces due to constant thermal motion of the molecules. The stress-strain properties of such a network of molecular chains can be calculated by statistical thermodynamical methods, and it is shown that, for a simple model, in which it is assumed that there is no interaction between the molecular chains except at the junction points and that the total force is due to changes in entropy, the equilibrium value of the stress (τ) required to extend a piece of rubber from its original length l_o to a final length l is given by the expression:

$$\tau = G\left\{\frac{l}{l_o} - \left(\frac{l_o}{l}\right)^2\right\},$$

where G is a constant depending on the number of network junctions per molecule and the molecular weight of the material.

It has already been mentioned that this theory has successfully accounted for the general shape of the stress-strain curves of vulcanizates of pure mixings; although strictly the theory should be applied only to equilibrium stress-strain data, it is found that a relation of the type given in the equation fits data obtained during slow speed stretching. At elongations greater than 300 per cent, the stress-strain curves determined on the natural rubber vulcanizates show a much more rapid increase of stress with strain than is given by this relation; this discrepancy has been attributed to the occurrence of crystallization, in which case the simple model used as a basis for the kinetic theory is obviously no longer true.

As is to be expected, the normal tensile stress-strain curves obtained with vulcanizates containing fillers no longer show close agreement with the equation; indeed, in strongly reinforced vulcanizates, the majority of the force required to stretch the rubber is not due to the resulting changes in entropy. Thus the interpretations of workers[2] who have attempted to account quantitatively for the behavior of reinforced vulcanizates, using the conclusions of the kinetic theory, are based on specious foundations.

Considerable changes in the mechanical properties of rubber may result from previous stretching; by far the largest changes are caused by the first extension, and the differences between the properties before and after subsequent extensions get progressively smaller until, after five or six extensions, there is but little difference between the results obtained in successive stretches. Although numerous workers have studied the initial and subsequent stress-strain curves, there has been a general lack of complete appreciation of the unique nature of the initial stress-strain curve. Bouasse[3], Gerke[4], and Williams[5] all endeavored to obtain reproducible and reversible stress-strain curves by subjecting their samples to repeated stretching or by pounding them in the stretched state, and Holt[6] suggested that it was more valuable to study the succeeding curves from both a theoretical and a practical point of view. The deficiencies

of the initial stress-strain curve to characterize a rubber have been emphasized by Vogt[7], but there has been no detailed study of the progressive changes in properties with stretching.

I. EFFECT OF PREVIOUS STRETCHING ON TENSILE STRESS-STRAIN PROPERTIES

(1) EXPERIMENTAL DETAILS

The compounding details of the mixes used are given below; these mixes were selected as likely to show a range of physical properties. Throughout this investigation normal tensile tests were carried out on a Scott tensile testing machine, and Type C dumb-bell test-pieces of the dimensions recommended in B.S.903-1940 were stretched at the standard rate of 20 inches per minute, measurements made during the test showed that the actual gauge length of the test-piece was extending at approximately 10 inches per minute.

Ingredient	Mix A	Mix B	Mix C	Mix D	Mix E
Smoked sheet rubber	100	100	100	100	100
MPC carbon black	—	50	—	—	—
Whiting	—	—	60	—	—
Colloidal china clay	—	—	—	60	—
Finely divided amorphous silica	—	—	—	—	40
Magnesium carbonate	—	—	—	80	—
Iron oxide	—	—	—	1	—
Zinc oxide	5	5	6	5	4.9
Stearic acid	1	2.5	3	2	1
Pine tar	—	4.5	2	—	4
Parafin wax	—	—	—	1	—
Brown substitute	—	—	—	8	—
Antioxidant	—	—	1	—	1
Mercaptobenzothiazole	—	0.8	—	—	—
Dibenzothiazyl disulfide	—	—	1	1	—
Diphenylguanidine	0.75	—	0.4	0.2	—
Vulkacit-AZ	—	—	—	—	0.8
Sulfur	3	3	2.5	3	2.5
Vulcanization	30 min. at 50 lbs.	30 min. at 50 lbs.	15 min. at 40 lbs.	30 min. at 40 lbs.	30 min. at 50 lbs.

(1) *Effect of the magnitude of the previous stretch*

Normal tensile tests were performed on samples which had not been previously stretched and on samples which had been stretched first to approximately one-quarter, one-half, and three-quarters of their breaking elongation, then immediately released and, starting within 30 seconds, stretched to break. Figure 1 shows the results of some of these tests. Usually some residual elongation or set was present before the commencement of the second stretch; in these cases it was considered that the actual elongation in the second stretch was approximately equal to the difference between the elongation measured with reference to the initial gauge marks and the set. In Figure 2 the set, present before the recording of the second stress-strain curve, has been subtracted from the elongation measured with reference to the original markings on the test-piece, and appropriate corrections have been made to the stress for the reduction in the cross-sectional area produced by the set.

The differences between the curves in Figures 1 and 2 are obvious only in cases where the set was large; correction for the set in this way does not

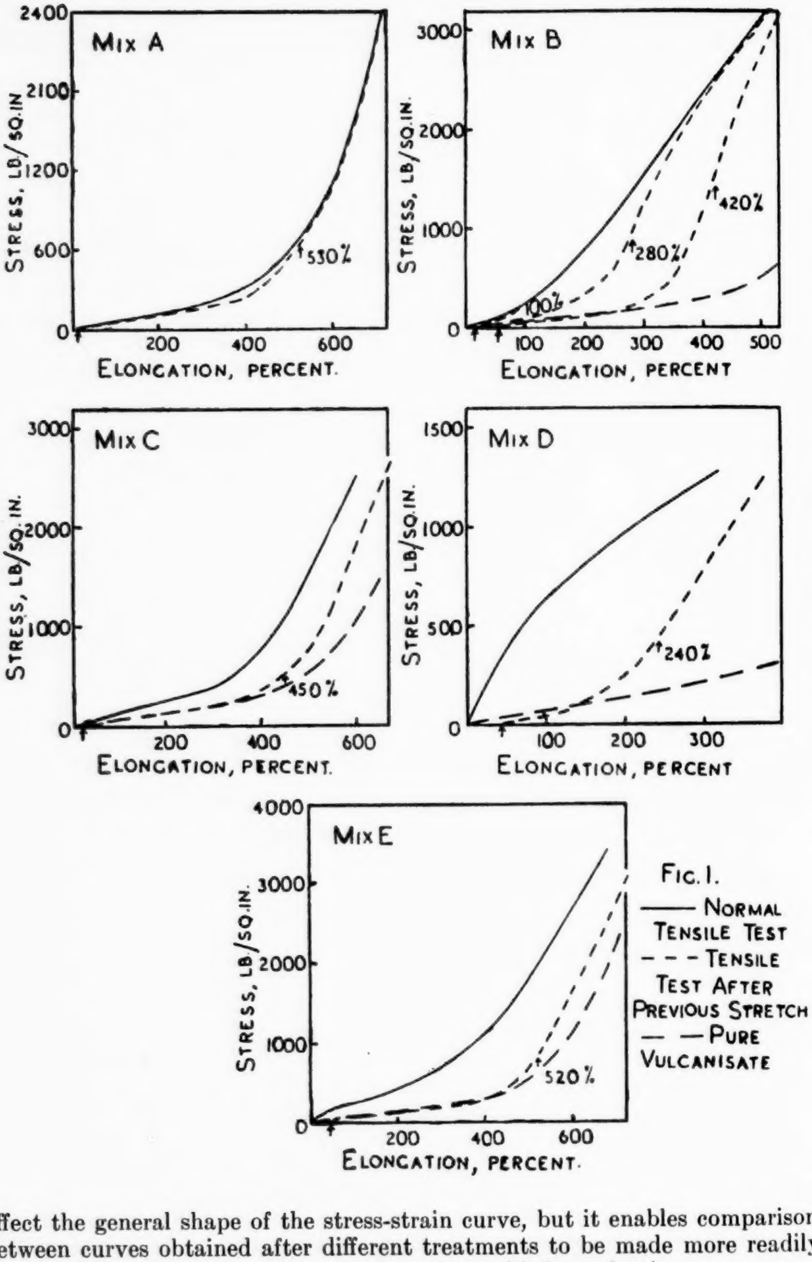


Fig. 1.
—— Normal Tensile Test
- - - Tensile Test After Previous Stretch
— — Pure Vulcanisate

affect the general shape of the stress-strain curve, but it enables comparisons between curves obtained after different treatments to be made more readily, and this correction has been made throughout this investigation.

These results show that previous stretching has relatively little effect on the stress-strain properties of the vulcanizate of the pure natural-rubber mixing (Mix A), but in all the other vulcanizates considerable softening is produced at elongations less than the previous stretch the degree of softening being

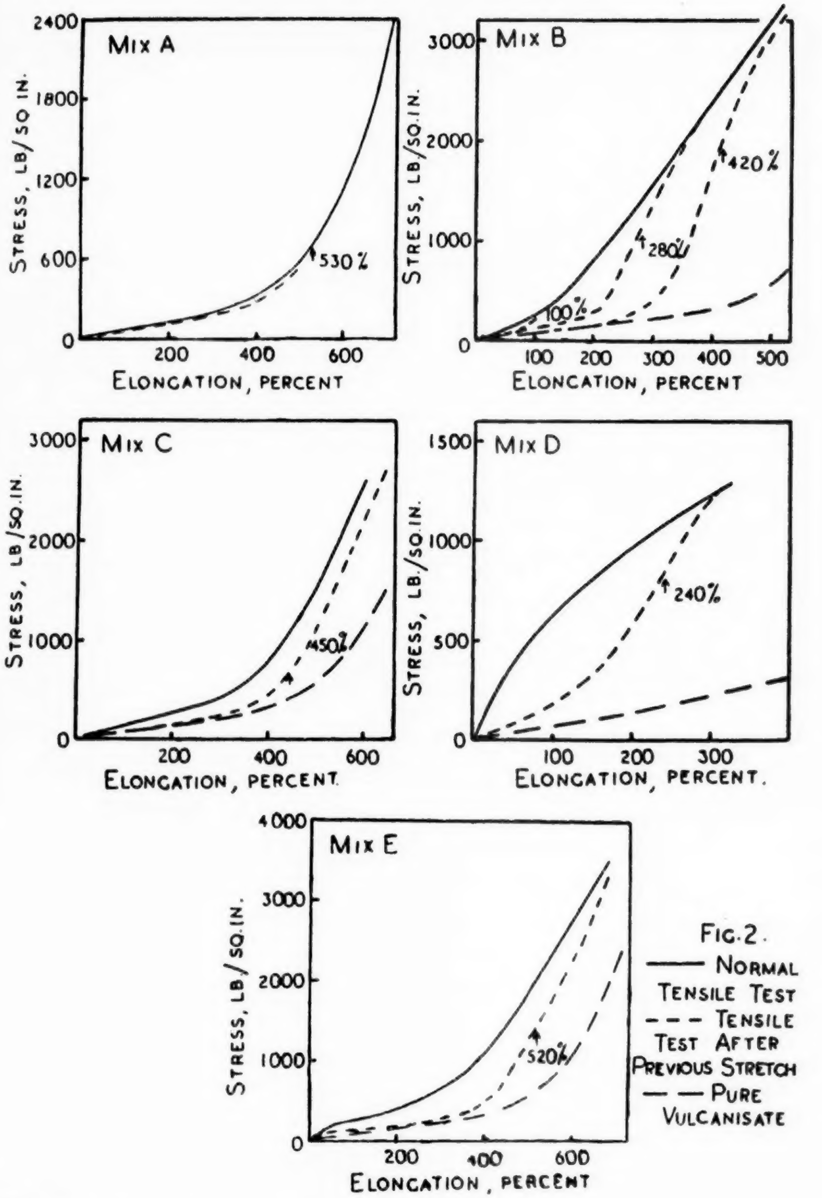


Fig. 2.

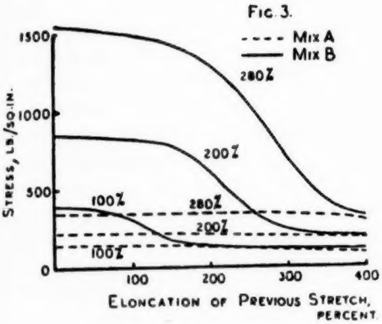
greater the greater the stiffening effect of the filler. It also appears that considerable softening is present only at elongations less than the previous stretch, and at elongations in excess of the previous stretch the behavior of the rubber is approximately as if there had been no previous stretch, although there is a small softening present at elongations slightly in excess of the previous stretch elongation.

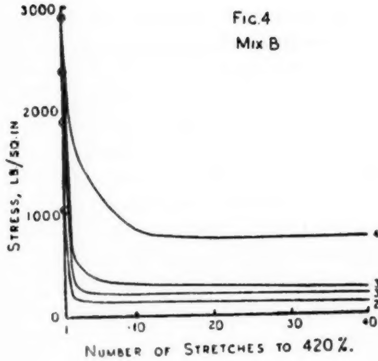
The stress-strain curve of the pure vulcanizate (Mix A) is also shown in each of the graphs in Figure 2. Comparison of the curves for the vulcanizates, containing fillers, which have been previously stretched, and the pure vulcanizate shows that when samples have been previously stretched their stress-strain properties approach those of the pure base vulcanizate at elongations less than about one-half of the previous stretch elongations. It thus appears that at these elongations the increase in stiffness produced by the incorporation of fillers or reinforcing agents is substantially destroyed by stretching. Conover[8] reported that, for vulcanizates containing fillers, the area under the stress-strain curve during retraction, *i.e.*, the energy returned, was practically independent of the kind or amount of the filler. Although Barron and Cotton[9] did not completely confirm this conclusion, they showed that the increase in the energy returned during retraction, produced by the addition of reinforcing fillers, was small compared to the increase in the energy required for extension. These observations agree with those put forward here, and can now be interpreted in terms of the destruction of the stiffening effect of the filler during the first stretch so that subsequently it behaved largely as an inert filler.

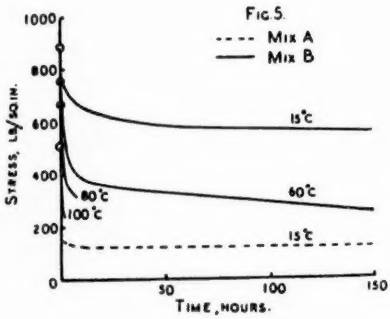
A second noticeable feature is that the course of any part of the stress-strain curve is substantially unaffected by previous stretching which has not reached this part; this is due to the fact, that at any given elongation, even in the initial stress-strain curve, the majority of the bonds produced by the filler, which affect the stress required to produce a lower elongation, have already been destroyed, and thus the stress required to produce a greater elongation is mainly controlled by bonds which are destroyed only at greater elongations. Pronounced differences between those rubbers which have not been previously stretched, and those which have been previously stretched, are only shown at elongations similar to, or less than, that of the previous stretch. A simile may help here; stretching the rubber can be compared to taking a cross-country tramp along an overgrown track; progress will only be easy in parts which have recently been used and where the undergrowth is broken down.

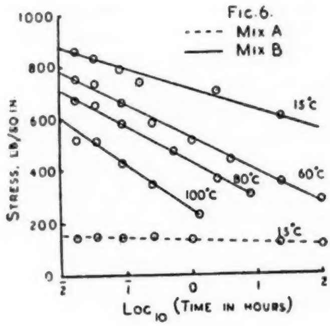
In a closer study of the effect of the magnitude of the elongation of previous stretches on the subsequent stress-strain properties, the stress required to extend dumb-bells of both the pure (Mix A) and the tread (Mix B) natural rubber vulcanizates to either 100, 200 or 280 per cent elongation was measured on samples during the initial stretching and after they had been previously stretched to various elongations from 50 to 400 per cent. As it was desired to measure approximately equilibrium values of the stress, the samples were stretched for 5 minutes, then allowed to recover for 5 minutes, and then the stress measured after 5 minutes at the subsequent elongation. The stress required to extend the test samples to a given elongation fell rapidly at first and then more and more slowly, and as a compromise, the stress was measured after 5 minutes when the rate of fall of stress was comparatively slow.

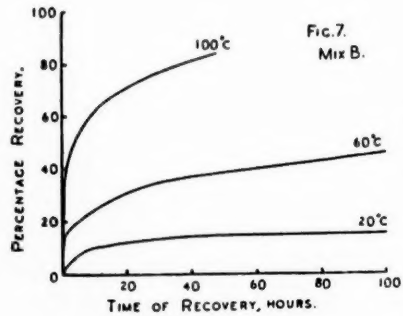
The results are shown in Figure 3; here the curves clearly show the small effect of previous stretches to low elongations on the stress required to produce a high elongation, and the almost complete destruction of the stiffening effect of the black at elongations less than about one half the elongation of the previous stretch. For example, a previous stretch to an elongation of 200 per cent results in only a small reduction in the value of the 280 per cent stress, but it results in a large proportionate reduction in the value of the 100 per cent stress. It is of interest to note that the position of maximum slope of these curves approximately corresponds to the selected elongation; the shape of these curves will be discussed more fully in the second part of this report.

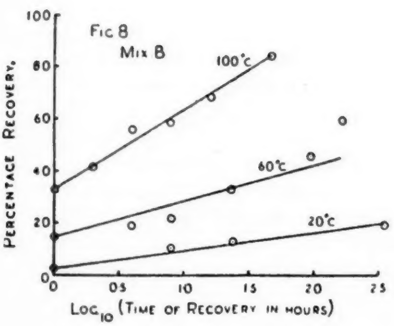












(2) *Effect of repeated stretching*

It has already been mentioned, that the first extension produces much larger changes in the stress-strain properties of rubber than subsequent extensions. Figure 4 shows results of normal tensile tests obtained during repeated extension to 420 per cent elongation (approximately three-quarters of the breaking elongation) on the natural-rubber tread vulcanizate (Mix B); it shows the changes in the stresses required to extend the dumb-bell test-pieces to 200,

300, 350 and 420 per cent during repeated extension to 420 per cent. These results confirm that during repeated extension the rubber rapidly settles down to a state where there is but little difference between the results obtained in successive stretches. Further, when this state is reached, the tread vulcanizate has stress-strain properties very similar to those of the pure vulcanizate at elongations less than the elongation of the previous stretch.

The progressive nature of the breakdown of the stiffening action of the filler with repeated stretching is to be expected, as in any one cohesive bond the force occurring changes with each repetition of the stretch, due to changes in the orientation of the bond. Thus, if the probability of breakdown of the stiffening action introduced by the filler, at any selected elongation, during the first stretch is the fraction P, then the fraction $1 - P$ remains after the first stretch; if the second stretch is similar to the first stretch then the fraction remaining after the second stretch is $(1 - P)^2$, and after n similar stretches, $(1 - P)^n$. Thus the forces required to produce subsequent stretches grow progressively smaller; a process of this nature is of a simple exponential form, as the breakdown during any elongation is proportional to the stiffening action of the filler which remains.

The curves in Figure 4 show the effect of repeated stretching to 420 per cent elongation on the stress required to produce selected intermediate elongations, *i.e.*, 420, 350, 300 and 200 per cent, these curves show only slight departures from this simple exponential behavior, although there is evidence that, as would be expected, the value of P decreases as the number of stretches increases.

The value of the fraction P also depends on the magnitude of the previous stretches, together with the selected elongation at which P is being measured. Figure 4 shows clearly that the value of P is almost unity when this selected elongation is much smaller than the previous stretch elongation, *i.e.*, breakdown is almost complete during the first strech, and that the value of P decreases as the ratio of the selected elongation and the previous stretch elongation increases.

(3) *Relaxation of stress during stretching*

Repeated stretching substantially destroys the increase in stiffness produced by the incorporation of fillers or reinforcing agents; it thus appears reasonable that much of the relaxation of stress which occurs in strongly reinforced vulcanizates during subjection to a constant tensile strain may be due to a similar breakdown of the stiffening structure.

Dumb-bell test-pieces of both the pure (Mix A) and the tread (Mix B) natural-rubber vulcanizates were stretched to both 100 and 200 per cent elongations at 15°, 60°, 80° and 100° C, and the gradual relaxation of stress while the samples were maintained at the constant elongation was observed with the aid of a lever arm pivoted at a fulcrum with the test-piece at one end and balancing weights at the other.

The relaxation of stress at 200 per cent elongation of samples of both mixes is shown in Figure 5, the initial measurements being taken one minute after starting. Figure 5 only shows the results of the stress relaxation of the pure vulcanizate at 15° C, as the curves obtained at 60° and 80° C almost coincide with that obtained at 15° C. After an initial rapid fall in stress, the samples settled down and the stress falls steadily; the rate of stress relaxation is very much greater in the black vulcanizate than in the pure vulcanizate at the corresponding temperature and elongation, and is much accelerated by increase in

temperature. At the highest temperature employed, however, the combination of heat and strain produced rapid aging, and the tests had to be terminated after a short period of relaxation, while at normal temperatures the rate of stress-relaxation was slow and protracted experiments will be necessary to indicate the course of the relaxation. However, the results obtained at 60° and 80° C suggest that the stress-relaxation occurring in the tread vulcanizate at these temperatures is largely due to the breakdown of the stiffening structure. The tests at these temperatures were also terminated when it was considered that aging might begin appreciably to modify the stress-strain properties of the rubbers. The results at 15° C show also the importance of the breakdown of the stiffening structure, but here the rate of breakdown is much slower.

Normal tensile tests performed on the samples after stress relaxation showed that, at elongations greater than the relaxation elongation, the stress-strain properties were substantially those of the original unstretched vulcanizate, but at lower elongations, the rubber had softened considerably; these suggest that the stress-relaxation of the loaded vulcanizate is largely due to a breakdown similar to that produced by previous stretching, as the stress-strain properties had not been appreciably modified by the continued extension.

The results shown in Figure 5 are given again in Figure 6, but here the period of stretching is plotted on a logarithmic scale; these curves show a linear dependence of the stress on the logarithm of the time over the range examined, and show the continuous nature of the stress-relaxation process.

(4) *Anisotropic properties produced by stretching*

The results of tensile tests showed that, although stretching reinforced vulcanizates produced softening in all directions throughout the rubber, the degree of softening was not the same in all directions, and anisotropic stress-strain properties, *i.e.*, grain effects, were developed. Tensile stress-strain tests were performed on dumb-bell samples, cut from a large sheet of the natural-rubber tread vulcanizate (Mix B), before and after the sheet had been stretched. The dumb-bells, which were cut both along and perpendicular to the direction of stretch, were cut from the central region of the sheet. Measurements showed that here the ratio of the dimensions of the stretched and unstretched sheet in the direction perpendicular to the direction of stretch was approximately equal to the reciprocal of the square root of the ratio of the stretched and unstretched dimensions in the direction of stretch and thus, assuming there is no volume change during the stretch, that in this region the sheet was free and substantially uninfluenced by the restrictions imposed by clamping the ends of the sheet.

Comparison of the results of the tests showed that, although tensile stretching produced softening in both of the selected directions, softening in the direction perpendicular to the direction of stretch was less than half the softening produced in the direction of stretch.

The anisotropy of the stress-strain properties resulting from stretching was convincingly confirmed by the results of swelling tests performed on stretched and unstretched samples of the natural-rubber vulcanizates. It is well known that, for rubbers made from the same polymer, the stiffer the rubber the less the swelling; this fact enables the results of swelling tests to be interpreted in terms of stiffness.

In these tests the overall dimensions of dumb-bell test-pieces were measured before and after various periods of immersion in xylene; the tests were continued

until the samples were fully swollen (10 days at 25° C). Measurements were made on dumb-bells which had not been previously stretched and on dumb-bells which had been stretched and then immediately released six times to approximately three-quarters of their breaking elongation.

The ratios of the fully swollen and the unswollen dimensions of the pure and the tread natural-rubber vulcanizates are given in the table below; the results quoted are the means of measurements on duplicate samples and on the samples to be stretched, the unswollen measurements were made before stretching.

	Swollen length / Original length	Swollen breadth / Original breadth	Swollen thickness / Original thickness	Swollen volume / Original volume
Unstretched				
Pure mix (Mix A)	1.7(0)	1.7(2)	1.7(2)	5.0
Tread mix (Mix B)	1.4(8)	1.4(3)	1.5(0)	3.2
Stretched				
Pure mix (Mix A)	1.7(4)	1.6(8)	1.6(4)	4.8
Tread mix (Mix B)	1.7(4)	1.2(9)	1.3(0)	2.9

In both cases the unstretched rubbers show isotropic swelling behavior; as is to be expected, the tread vulcanizate has swollen to a less degree than the pure vulcanizate. With the stretched rubbers, the pure base vulcanizate still shows substantially uniform and similar swelling, the rubber being, if anything, slightly softer in the direction of stretch than in other directions; the tread vulcanizate, however, shows pronounced changes resulting from stretching; it is much softer in the direction of stretch than in other directions. It is of interest that the volume swelling is not greatly affected by the stretching, and thus the increase in swelling in one direction is also associated with a decrease in swelling in other directions, and thus the reduction of the swelling ratios in the directions at right angles to the length which result from stretching can readily be explained, although at first sight they appear to contradict the observed tensile softening in these directions. The slight decrease in volume swelling which results from stretching appears to be significant.

To investigate the effect of severe straining in all directions on the swelling, test-pieces 1 inch square were cut from a 0.1-inch sheet, and slowly passed through the nip of a mill several times, the nip being set so that it compressed the 0.1-inch sheet to 0.05 inch. After recovery, swelling tests were performed; these showed that when correction had been made for the volume of black present, the volume swelling was almost exactly that of the pure vulcanizate; further, the linear swelling ratios were similar in all directions.

The results of similar tests performed on the other natural-rubber vulcanizates showed that, in some cases, anisotropy of swelling properties already exists in the unstretched vulcanizate; this was particularly evident in Mix D, which contained magnesium carbonate and colloidal china clay as fillers; but again, in all cases, an increase of swelling is produced in the direction of stretch. These results clearly demonstrate the breakdown of stiffening structure during stretching and the anisotropic properties which result from this breakdown.

(5) *Recovery of the original tensile properties after stretching*

To understand the softening produced by stretching more fully, and also to assess its practical significance in service applications, it is important to know whether the rubber readily recovers to its initial state, and if so, the rate

at which it recovers and the dependence of this rate on conditions such as temperature. Tensile tests were therefore performed on samples, of both the pure (Mix A) and the tread (Mix B) natural-rubber vulcanizates, which had been stretched firstly to 420 per cent elongation, then released, and allowed to recover for various periods at both normal and elevated temperatures. In tests where the recovery took place at an elevated temperature, the samples were cooled before the tensile tests were performed.

Figure 7 gives some of the results for the tread mix (Mix B); here the stress required, after various periods of recovery, to produce 200 per cent elongation on samples which had been previously stretched has been used to determine the degree of recovery towards the initial stress-strain curve. It will be remembered that immediately after prestretching to 420 per cent the stress required during a subsequent extension to produce an elongation of about 200 per cent or less is very similar to that required by the pure vulcanizate (Mix A).

The figure shows that even after a prolonged period at 20° C only a small recovery of the stress-strain properties has taken place. On the other hand, two days at 100° C was sufficient for samples to recover nearly to their original stress-strain properties; longer periods of recovery at this high temperature were not undertaken, since there was evidence that the stress-strain properties of control samples were slightly modified as a result of this aging.

Unfortunately, as in earlier stress-relaxation tests, it has not been possible to show the limit of recovery, since at high temperatures aging is a contributory factor and at low temperature the process is very slow. Figure 8 again shows how the percentage recovery increases with the period of recovery; here the time is plotted on a logarithmic scale, and again as in the stress-relaxation tests, the recovery is proportional to the logarithm of the period of stretching, and thus the data suggest that in all cases the recovery was still continuing steadily when the tests were stopped.

From most practical points of view, the softening of this tread vulcanizate produced by previous stretching is of a permanent nature, since at normal temperatures recovery towards the initial stress-strain properties is very slow, whereas if the rubber is used at high temperatures, then recovery is more rapid.

(6) *Effect of previous stretching on the tensile strength*

So far the effect of previous stretching on the tensile strength and the elongation at break has not been discussed; it has been reported[10] that the tensile strength is normally reduced as a result of repeated stretching, and stretching a number of times to a relatively low elongation has the same effect as stretching fewer times to a higher elongation. Results obtained during numerous tests on all five vulcanizates used in the present investigation showed no evidence of any significant change in the value of the tensile strength as a result of previous stretching after corrections had been made for the reduction in cross-sectional area caused by set. The elongation at break of samples showing considerable set after stretching was normally greater on samples which had been previously stretched than on unstretched samples; however, when the set present immediately before the test was subtracted from the observed elongation at break, the results approached the elongation at break of samples which had not been prestretched.

The effect of correcting for set during a comparison of tensile strength data obtained before and after previous stretching is clearly shown in the following table. Here the first two columns give the tensile strength and breaking elonga-

tion calculated on the original dimensions of the test-piece; the last two columns give their values calculated on the dimensions after previous stretching, but before testing.

	Calculated on original dimensions			Calculated on dimensions after previous stretching	
Mix	Tensile strength (lbs. per sq. in.)	Breaking elongation (%)	Set (%)	Tensile strength (lbs. per sq. in.)	Breaking elongation (%)
A	2740	690	8	2810	682
B	3305	550	32	3510	518
C	2640	675	20	2725	655
D	1235	380	50	1410	330
E	3100	730	50	3330	680

It thus appears that in cases where a lower tensile strength results from previous stretching, the effect is due either to the generation of small tears during the earlier stretches, which causes a reduction in the breaking strength, or to the reduction of cross-sectional area of the test-piece resulting from set.

(7) *Conclusion*

The tensile stress-strain properties of pure natural-rubber vulcanizates are affected only slightly by previous stretching; on the other hand, vulcanizates containing reinforcing agents, or fillers which stiffen the rubber, may on second stretching be considerably softer at elongations less than the elongation of previous stretches. The original increase of stiffness at these elongations produced by the incorporation of reinforcing agents or fillers is thus destroyed by repeated stretching.

From most practical points of view, this softening is of a permanent nature, for at normal temperatures the recovery towards the initial stress-strain properties is very slow.

The major portion of the relaxation of stress which occurs in strongly reinforced vulcanizates when they are continuously extended to a constant elongation is also due to the destruction of the increase in stiffness produced by the reinforcing filler.

Although it must be emphasized that the majority of this investigation has been on two vulcanizates, one a pure and the other a tread (channel black) natural-rubber, in all cases where other vulcanizates containing different polymers and different fillers, including a range of channel, furnace, and thermal blacks, were investigated, the differences observed were only in detail and did not modify the major conclusions. Therefore, it is considered that the conclusions are of a general nature and apply to most vulcanizates containing strongly reinforcing fillers. Results of tests in compression also show softening of rubber vulcanizates at compressions less than that of previous compressions.

II. DISCUSSION OF RESULTS

(1) THERMODYNAMICAL CONSIDERATIONS

As has already been mentioned, the kinetic theory of rubber elasticity assumes that the tension in stretched rubbers is associated only with the entropy of the material, and thus in the following general thermodynamical equation, which gives the tension (σ) during reversible isothermal stretching; $\sigma = (\delta F/\delta L)_T = (\delta U/\delta L)_T - T(\delta S/\delta L)_T$, it can be assumed that $(\delta U/\delta L)_T = 0$ or $\sigma = -T(\delta S/\delta L)_T$, where F, U, S, L and T are the free energy, internal energy, entropy, length, and absolute temperature, respectively.

Although the results of the slow-speed stretching discussed are not equilibrium data, and therefore, these thermodynamical considerations should not be applied rigorously, several valid conclusions can be drawn from studying the results in this way.

Experimental results for the slow-speed stretching of pure rubbers show that the assumption that the tension depends only on the entropy of the material, is substantially correct and thus, in these cases, there can be little deformation of the chemical bonds which exist, or other changes which lead to a change in internal energy. However, departures from this behavior are serious when reinforced vulcanizates are used, or when pure vulcanizates are stretched to high elongations.

The similarity of the stress-strain curves of all the vulcanizates after previous stretching at elongations less than the previous stretch elongation, and their fairly close agreement to the conclusions of the kinetic theory (see Figure 1), suggests that in these cases there is little change in internal energy during stretching.

However, during the first stretches of reinforced vulcanizates, two processes occur; an increase in the internal energy, due to the breakdown of the stiffening structure and to the increase in surface area, which results from its breakdown, together with a decrease in entropy, due to the changed molecular configuration. (The breakdown of structure will, however, lead to an increase in entropy because of the consequent increased mobility or number of possible configurations of the chains.) These two processes are additive and provide two components of the force required to stretch the rubber. Once the structure is broken down, large forces are no longer required to move the molecules during subsequent extensions.

The stress-relaxation data which have been reported here indicate that the value of the true equilibrium stress required to extend a reinforced rubber to a given elongation may be similar to the stress required to stretch a similar vulcanizate, but with an inert filler as a diluent, to the same elongation. If this is the case, the kinetic theory of elasticity accounts for the limiting equilibrium value of the stress; at normal temperatures, this is reached only after long periods of deformation. On the other hand, repeated stretching or stretching once to an elongation greatly in excess of the test elongation rapidly brings about this state.

Hysteresis loops formed by stress-strain curves during extension and retraction show this phenomenon in a somewhat different way. Figure 11 shows hysteresis loops obtained by Holt[6] during slow-speed stretching and retraction of both pure and tread natural-rubber vulcanizates; the curves shown were recorded for ring shaped samples during the initial and the fifth stretch. The area of the hysteresis loop, which gives the energy dissipated during any one cycle, is the sum of the following energy losses; (1) losses due to irreversible flow; (2) simple frictional losses; (3) losses due to the time dependence of the high-elastic deformation; (4) energy absorbed in the destruction of structure. In the normal slow-speed stretching of vulcanized rubber, both of the components (1) and (2) are relatively small; while the component (2) does not vary greatly with repeated stretching. Comparison of the hysteresis loops recorded during the first and fifth stretch shows the large amount of energy required to break down the stiffening structure in the tread vulcanizate during the first stretch.

In subsequent stretches the area of the hysteresis loop decreases rapidly as the structure is progressively broken down. Thus if energy losses due to

causes (1), (2) and (3) were absent, the limiting forms of both the extension curve and the retraction curve would be the same. The curves for the pure vulcanizate show a slight breakdown of structure during repeated stretching.

In a number of physical tests on rubber vulcanizates, it is usual to condition mechanically the sample by taking it through several test cycles before measurements are made; this procedure enables reproducible results to be obtained in successive tests. The work described here indicates that such a procedure leads to the breakdown of some of the structure which may be present; for example, in the tensile tests described the differences between the first large hysteresis loop and subsequent loops is due mainly to the energy absorbed in the destruction or the structure and, as the number of cycles increase, the hysteresis loops progressively reproduce each other more closely.

(2) BREAKDOWN OF STRUCTURE

The effects produced by the introduction of reinforcing agents or fillers can be analyzed in a more formal way if it is assumed that the increase in stiffness is due to the existence of cohesive bonds (at this stage there is no need to postulate the exact nature of these bonds, or whether they exist between filler-filler particles or ruber-filler particles). Such an analysis must account for: (1) the progressive breakdown of bonds as the magnitude of stretch is increased; (2) the cumulative effect of repeated stretching; (3) the progressive breakdown of bonds during prolonged stretching.

A theory based on the following lines gives an adequate interpretation for these experimental observations.

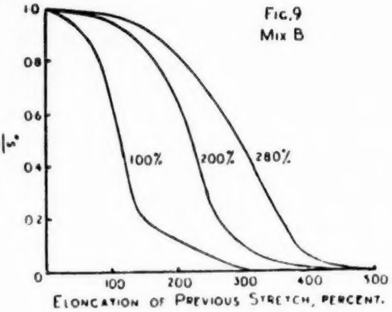
When a piece of rubber is stretched, the actual forces produced in the single bonds at any moment are distributed statistically about a mean value due to the random orientation and fluctuation of the bonds; thus, some of the bonds are subjected to large forces, whereas others are subjected to little or no force; further, the force exerted in any one bond varies continuously with time, and with each repetition of the stretch. The strength of the bonds is also distributed statistically over a range of values, and a bond is broken during stretching if the force developed in it is greater than its strength.

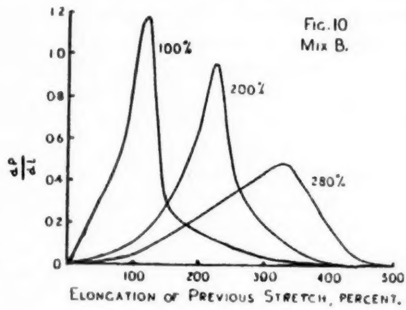
The increase in stiffness which results from the incorporation of reinforcing ingredients has already been attributed to the presence of cohesive bonds; thus the stress required to extend the rubber to a given elongation depends on the number and strength of these bonds. A completely inert filler incorporated into the rubber would, however, cause a slight increase in stiffness, even in the absence of cohesive bonds; but here we are interested in a much larger increase in stiffness due to active fillers. Considering the decrease in stress required to produce a fixed elongation which results from previous stretching, the fractional decrease in the component of the stress introduced by the reinforcing ingredient is given by the expression: $1 - S/S_o = \Psi P$ where S_o is the original component of stress due to the cohesive bonds, and S is this component of stress after the breaking of a fraction P of the bonds.

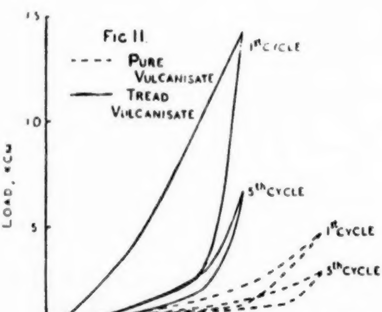
Figure 9 shows data, originally given in Figure 3, replotted to show the change in the function S/S_o, with the magnitude of the previous stretch elongation, at three selected elongations. To obtain the value for the component of stress due to the bonds, it is necessary to know the stress-strain properties of a similar mix, but with an inert instead of an active filler; for the purposes of this calculation, the stress-strain properties of the loaded vulcanizate after a large number of repeated stretchings were employed.

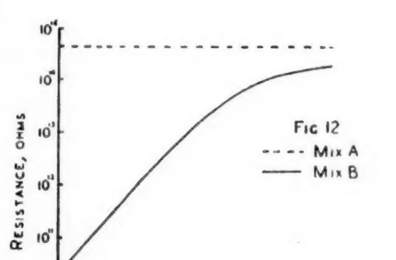
If, now, it is assumed that the stress required to extend the rubber is proportional to the number of cohesive bonds present, then $1 - S/S_o = P$.

Figure 10 shows curves of $d(1 - S/S_o)/dl$ or dP/dl against the previous stretch elongation l; the ordinate is equivalent to the lumped frequency of occurrence of bonds which contribute to the component of stress introduced by the filler. An interesting feature of the shape of these frequency-distribution curves is the relatively small contribution which is made to the stress at a particular elongation by the bonds which rupture at much higher elongations; this feature can also be seen by a study of the curves in Figures 2 and 3, and is thus not dependent on the assumptions made in obtaining the curves in Figure









10. This indicates that either: (1) many more bonds are broken at low elongations than at high elongations; (2) different bonds contribute differently to the total stress at a given elongation, those breaking only at high elongations contributing little to the stress at low elongations. For example, it is possible that, due either to their nature or orientation, different bonds may have different stress-elongation relations.

If this second theory is correct, the stress is obviously not simply proportional to the number of bonds present, and the curve in Figure 10 can no longer be identified with a frequency-distribution of occurrence of bonds.

As yet, it has not been possible to differentiate conclusively between these two theories, although the following evidence suggests that (2) may be relatively unimportant.

The portions of stress-strain curves at elongations in excess of the previous stretch elongation are very similar in all cases, whether the sample has not been previously stretched, whether it has been repeatedly stretched, or whether it has been stretched continuously for a long period. In these last two cases, the stress in any one bond varies continuously with time, due to either repeated stretching and retraction or to prolonged thermal agitation. Thus it would appear that the majority of weak bonds are at some instant subjected to stresses sufficiently large to break them; in this case the majority of bonds breaking at high elongations are strong bonds.

The cumulative effect of repeated stretching has been discussed earlier in this report; it was then indicated that the probability of breakdown of bonds decreased slightly with successive stretches; the cause of this can now be interpreted in terms of the probability of breakdown of bonds. The distribution of bond strengths alters its form during each stretch as a result of the presence of relatively fewer weaker bonds after stretching than before stretching, and the probability of breakdown of one of the remaining bonds decreases as the number of stretches increases. A result of the progressive decrease in probability of breakdown is that the differences between successive stretches are not so great, and the limiting value of the stress is approached more slowly.

This argument has been developed for tests in which the samples are subjected to the same elongation. If, however, the same force is applied at each loading, the average stress intensity on each bond increases with each successive stretch as progressively fewer bonds remain to support the force.

In this analysis, the continuous breakdown of bonds during prolonged stretching has not yet been considered; however, it has been indicated that the stress in any one bond varies continuously with time, as a result of thermal agitation. Thus on stretching, all the breakdown does not occur instantaneously, and the bonds can be considered to have a finite life, being broken sooner or later by the forces produced by stretching and by thermal agitation; this process results in a continuous decay of stress. If, during this stress decay, the number of bonds broken in a given short interval of time is proportional to the number of bonds still unbroken, and the stress is proportional to the number of bonds present, then the stress S at a time t is given by $S_{(t)} = S_1 e^{-t/\tau} + S_2$ where τ is the mean life-time or relaxation time of the bond, and S_2 is the limting value to which the stress decays.

The results of the stress decay tests shown in Figures 5 and 6 do not behave according to a simple law of this form; indeed, it was shown that over the range considered in the stress decay tests the stress was proportional to the logarithm of the period of stretching. This lack of agreement was not unexpected, as the behavior of the bonds is most probably governed by a distribution of relaxation times and then: $S_{(t)} = S_1 \int_0^\infty f(\tau) e^{-t/\tau} d\tau + S_2$, and, over a limited range, an expression of this form may closely approximate to the logarithmic dependence of the stress on the period of stretching.

It is of interest to note that repeatedly stretching a sample to a selected elongation is a much more rapid way of breaking down these bonds than continuous extension to this elongation. This is due to the much more rapid movement of rubber molecules during extension and retraction than the movement due to normal thermal agitation

It is to be expected that, during the course of stress relaxation experiments, there will be a reformation of bonds akin to that which has already been shown

to occur in recovery tests. However, during stress relaxation experiments, this growth occurs while the sample is in its stretched state, so they do not greatly offset the stress required to maintain the sample to a constant extension.

Tobolsky and his coworkers[2] have developed a general theory of the stress relaxation and creep of rubbers at elevated temperatures which is based on the kinetic theory of elasticity; unfortunately, they have ignored the limitations which this imposes, and have used their theory to interpret the results on both pure and reinforced vulcanizates. It has already been emphasized that normally this is not justified; with a strongly reinforced vulcanizate may produce grossly misleading results. It must be mentioned, however, that much, although not all, of their work was performed at high temperatures, where apparently oxidative scission of primary bonds is the controlling process. A second important feature of their work which appears to demand investigation is the experimental technique of socalled intermittent stress relaxation or creep which they employ to isolate the scission reaction. In this technique, the sample is momentarily extended at the time of measurement, and remains unstretched at all other times; this is equivalent to repeated stretching, and it has been shown here that this results in a rapid decay in the stress required to extend the sample to a given elongation if strongly reinforced vulcanizates are used; although they employed reinforced vulcanizates, no such phenomenon is reported by them.

(3) DISCUSSION OF THE MECHANISM OF REINFORCEMENT

Although it is not possible to give an exact definition of the term reinforcement, it is generally agreed that reinforcement is the improvement of the physical properties of vulcanized rubber resulting from the incorporation of fillers. However, the improvement of any one property such as tensile strength, tear strength, abrasion resistance, or stiffness, does not mean that the vulcanizate is reinforced. Parkinson[11] has suggested that a filler should not be classed as a reinforcing agent unless it increases substantially both abrasion and resistance to tearing.

Numerous attempts have been made to explain the reinforcing action of fillers in rubber and, although the opinion of practically all rubber technologists is that reinforcement is due to either or both of the following processes: (1) interaction between the surfaces of the filler particle and the rubber; (2) flocculation of the filler particles into chainlike structures of aggregates, many diverse and sometimes contradictory opinions have been put forward. This unsatisfactory state has been emphasized in reviews by Shepard, Street, and Park[12], and more recently by Parkinson[13].

The results of this investigation, although not providing conclusive evidence of the mechanism of reinforcement, are relevant, and provide evidence which should assist a more critical appraisal of many of the opinions and suggestions hitherto put forward; furthermore, they provide a basis on which tentative suggestions of the nature of reinforcement can be formulated.

First the results show that the difference in the work of extension between reinforced and not reinforced vulcanizates, which was recommended by Wiegand[14] as an index of reinforcement, is a property which largely disappears after the first stretch, and thus it is desirable that some other more permanent property should be adopted as an index. Parkinson[13] has emphasized that the increase in stiffness which results from the incorporation of fillers is not necessarily an indication of reinforcement; but although all fillers produce a stiffen-

ing, it is most marked in those fillers to which reinforcing properties are normally attributed.

It is of interest to note that the increases in electrical conductivity, power factor, and stiffness which result from the incorporation of carbon black into a rubber mix have a number of common features. Stretching or flexing the rubber vulcanizate results in a decrease in all three properties, even when the blacks are not of the "conducting" type; and, after such treatment, the subsequent recovery towards the original stress-strain or electrical property is accelerated by an increase in temperature. Further, for moderate concentrations, the stiffness, the conductivity, and the power factor are all progressively increased by increased loading of black. These similarities suggest that the same black structure may be responsible for the increases in all of these properties. Unfortunately, no direct quantitative comparisons can be made between the results of the electrical measurements and the stress-strain measurements, but Figure 12 shows the progressive increase in the electrical resistance of the test length of a dumb-bell sample of the tread vulcanizate, *i.e.*, decrease in conductivity, with the previous stretch elongation. Here the resistance was measured after stretching six times to one of various elongations. It will be noted that, after stretching to large elongations, the resistance of the sample has almost increased to that of the pure vulcanizate.

Bulgin[15] and, more recently, Wack, Anthony, and Guth[16] in discussing the electrical conductivity of carbon black mixes, have indicated the necessity for carbon particles to form chains before appreciable conductivity is shown, and it is reported that electron microscope studies show coherent networks of contacting carbon particles in vulcanized black-rubber mixes[17].

Wack, Anthony, and Guth showed that, when rubber samples were held extended to a constant elongation, the relaxation of stress was accompanied by a decrease in resistance; this is to be expected, as the carbon black chains broken down by stretching reform again in the strained state and, though not contributing to the stress required to hold the sample extended, lead to increased conductivity.

An interesting technique of the heat treatment of carbon black stocks has been the subject of two patents[18]. In these patents it is claimed that if a carbon black master batch is allowed to stand at a high temperature before the incorporation of the vulcanizing ingredients, the vulcanized product has better abrasion resistance, hysteresis, and electrical resistivity than a similar conventionally mixed vulcanizate. This has been discussed by Parkinson[11], and is attributed to a rapid flocculation of the black during the high temperature trestment; subsequent remilling then disperses the black to a greater degree than is obtained without such heat treatment. These conclusions are in keeping with the observations given in the table below; measurements of the power factor and permittivity were made on the natural-rubber tread master

Treatment of master batch	Power factor (%) at 10^7 c.p.s.	Permittivity at 10^7 c.p.s.	Solubility in benzene
(1) After milling	4.3	5.3	Soluble
(2) As (1) and flexing	3.2	5.2	Soluble
(3) As (2) and heat treatment	8.1	5.4	Insoluble
(4) As (3) and remilling	2.3*	4.7*	Soluble
(5) As (4) and heat treatment	3.2	3.6	Insoluble
(6) As (5) and flexing	3.3	3.6	Soluble

* After the remilling the samples only recovered their dimensions slowly, due to their relatively low temperature after the few passes through the mill; these measurements were made before they had completely recovered, in all other cases rcovery was substantially complete.

batch after milling, after flexing, after subsequently standing for 24 hours at 100° C, after a few passes through the mill, after a further 24 hours' standing at the high temperature, and after further flexing. All the tests were performed at 20° C after the test-pieces had been allowed to cool for half an hour.

The table also includes data on the solubility in benzene of the master batch after its various treatments. These results should be compared with those made on vulcanized rubber, already reported in the section on the "Effect of previous stretching on tensile stress-strain properties"; here again, an apparently complete breakdown of black structure was produced by severe straining.

If the presence of chains of carbon particles leads to an increase in power factor or conductivity, then these results indicate that it is not necessary to have such chain structure before the master batch becomes insoluble, and suggest that carbon-to-rubber adsorption alone is sufficient to preclude dissolution. Furthermore, they make it to formulate a plausible mechanism of the processes involved in the dispersion of the black.

Ladd and Wiegand[17] have shown that, before incorporation into rubber, carbon black possesses a chain structure, and recently Dobbin and Rossman[19] have shown that mechanical treatment of blacks before their incorporation into rubber stocks leads to a change in those properties of the vulcanizate which are normally attributed to the presence of aggregates or chains.

It appears probable that, during the initial milling, these chains or aggregates are partially broken down. On standing after milling, both a carbon-to-carbon structure and a carbon-to-rubber structure are built up, and these lead to an increased power factor, conductivity and stiffness and decreased solubility. Remilling after this structure has been formed involves larger forces, due to the stiffening of the stocks, and results in a more complete and substantially irreversible breakdown of the carbon-to-carbon structure. However the carbon-to-rubber structure, which also is broken down, reforms on standing and again results in decreased solubility.

Although a kinetic Brownian type of motion of the carbon black particles or chains is apparently present in both vulcanized and unvulcanized rubber, it is restricted by the adsorption of the carbon on the rubber, and thus the physical properties of the rubber mix depend on the relative magnitudes of the two processes of carbon-to-carbon and carbon-to-rubber adsorption, which in turn depend on the mechanical and thermal history of the rubber.

These ideas can now be applied to the initial problem of the softening of rubber vulcanizates which results from previous stretching. The filler structure present, which involves to a greater or less degree both agglomerates and chains of filler particles and adsorption of the filler particles on to the rubber, can be broken down by stretching or flexing the rubber, and it appears that both of these types of structure lead to increased stiffness. After this breakdown, the structure reforms. If the straining is not severe, recovery is substantially complete; this is shown by the almost complete recovery of electrical, tensile, and swelling properties. There is also some evidence that the formation of filler structure in the strained state is responsible for much of the permanent set present after long period straining and then release. This interesting aspect of reinforcement is being investigated.

SUMMARY

The results of tensile stress-strain, stress relaxation, swelling, electric conductivity, and power factor tests show that the properties of pure vul-

canizates are only slightly affected by previous stretching or flexing; on the other hand, the properties of vulcanizates containing reinforcing agents, or fillers which stiffen the rubber, may be considerably changed by previous stretching. The increases of stiffness, electric conductivity, and power factor produced by the incorporation of the fillers are destroyed by flexing or stretching. From most practical points of view these changes are of a permanent nature, as at normal temperatures the recovery towards the initial properties is slow. These effects are attributed to the breakdown of both agglomerates and chains of filler particles, and the adsorption of the filler particles on the rubber.

ACKNOWLEDGMENT

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REFERENCES

1 Buist and Davies, *Trans. Inst. Rubber Ind.* **22**, 68 (1946).
2 Tobolsky, Prettyman and Dillon, *J. Applied Physics* **15**, 380 (1944); Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945); Stern and Tobolsky, *J. Chem. Physics* **14**, 93 (1946); Andrews, Tobolsky and Hanson, *J. Applied Physics* **17**, 352 (1946).
3 Bouasse and Carrière, *Ann. faculté sci. Toulouse* **5**, 257 (1903).
4 Gerke, *Ind. Eng. Chem.* **22**, 73 (1930).
5 Williams, *Ind. Eng. Chem.* **21**, 872 (1929).
6 Holt, *Ind. Eng. Chem.* **23**, 1471 (1931).
7 Vogt, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, p. 332.
8 Conover, *Ind. Eng. Chem.* **22**, 871 (1930).
9 Barron and Cotton, *Trans. Inst. Rubber Ind.* **7**, 209 (1931).
10 U. K. Admiralty, Ministry of Aircraft Production and Ministry of Supply, "Rubber in Engineering", H.M.S.O., London, **1946**, p. 70.
11 Parkinson, *Trans. Inst. Rubber Ind.* **16**, 87 (1940); **19**, 131 (1943).
12 Shepard, Street and Park, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, p. 380.
13 Parkinson, "Advances in Colloid Science", New York, **1946**, Vol. 2, p. 389.
14 Wiegand, *Ind. Eng. Chem.* **17**, 939 (1925).
15 Bulgin, *Trans. Inst. Rubber Ind.* **20**, 24 (1944).
16 Wack, Anthony and Guth, *J. Applied Physics* **18**, 456 (1947).
17 Ladd and Wiegand, *Rubber Age* (N. Y.) **57**, 299 (1945).
18 Gerke *et al.* (to U. S. Rubber Products, Inc.), U. S. patent 2,118,601 (1938); Firestone Tyre & Rubber Co., Ltd., British patent 493,552 (1938).
19 Dobbin and Rossman, *Ind. Eng. Chem.* **38**, 1145 (1946).

TENSILE STRENGTHS OF PURE GUM NATURAL RUBBER COMPOUNDS *

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Pure-gum natural rubber compounds rank high in order of tensile strength, and values of the order of 30 kg. per sq. mm. of the breaking cross-section[1] are attainable. This is similar to that found for textile fibers, and is within one order of magnitude of the strength of steel piano wire. Among other rubbers, Butyl and Neoprene give similar values in pure-gum compounds, and it is significant that they share with natural rubber the property of crystallizing on stretching. Other rubbers, such as the various copolymers of butadiene, are at least one order of magnitude weaker. The dependence of strength on crystallization is further emphasized by the effect of the temperature of test. This will be discussed in more detail below, but it may be noted here that, below $-70°$ C, rubber behaves as a typical brittle solid, breaking without much elongation, with a tensile strength of about 5 kg. per sq. mm. Above $-70°$ C, rubber becomes elastic and crystallizable by stretching, and its extensibility and tensile strength increase very rapidly[2]. A number of authors have pointed out the importance of crystallization, and an admirable discussion of the problem has been presented by Flory[3], who shows how the effect of the molecular weight of the raw rubber on the tensile strength of the vulcanizate can be understood on this basis. The purpose of the present paper is to extend this idea, and to use it to discuss the effects of cure and conditions of test on tensile strengths.

ESTIMATION OF DEGREE OF CROSS-LINKING

The investigation to be described below suggests strongly that one of the most important factors in determining the tensile strength of a vulcanizate is the degree of cross-linking. The method employed for the determination of this quantity was based on a measurement of the extension of a strip of rubber carrying a dead load and immersed in light petroleum for 24 hours, as previously described[4]. An alternative essentially equivalent method depends simply on measurements of the equilibrium swelling of the compound in benzene. If Q_m is the equilibrium swelling, and M_c the molecular weight between junction points, we have[5]:

$$\ln\left(1 + \frac{1}{Q_m}\right) - (Q_m + 1)^{-1} = \mu(Q_m + 1)^{-2} + \frac{\rho_r V_0}{M_c}(Q_m + 1)^{-\frac{1}{3}} \qquad (1)$$

where ρ_r is the density of the rubber, V_0 the molar volume of the liquid, and μ a constant. The usefulness of this equation depends on μ being either independent, or a known function, of M_c. Boyer and Spencer[6] have recently presented evidence that μ is not in general independent of M_c, but in the particular

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case of the swelling of natural rubber compounds in benzene, our evidence shows that μ is substantially constant. The data plotted in Figure 1 refer both to accelerated compounds and to straight rubber–sulfur compounds, and it is clear that there is no systematic departure from the theoretical curve. Further, the value of $\mu = 0.395$ used in computing the curve is in satisfactory agreement with the value of $\mu = 0.41$ found by vapor pressure measurements on rubber hydrocarbon[7]. Equation (1) may, therefore, be employed as an experimentally verified basis for computing M_c from swelling data. In view of the greater convenience and precision of this method, it has been generally employed. It must be emphasized that the method is not indiscriminately applicable, *e.g.*, although the swelling of accelerated compounds in light petroleum follows Equation (1), that of rubber–sulfur compounds does not, presumably due to their higher combined sulfur content.

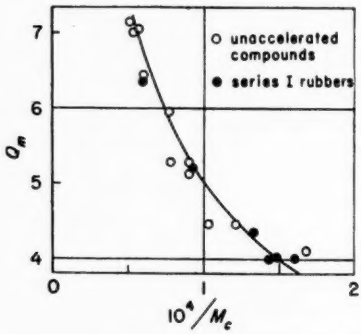

FIG. 1.—Dependence of maximum swelling (Q_m) on cross-linking; curve calculated from equation (1) with $\mu = 0.395$.

A semiempirical method which is useful in evaluating data reported in the literature is based on the observed connection between $10^4/M_c$ and the load per unit area of the unstretched rubber required to produce a given elongation, say 300 or 500 per cent. This quantity is widely used for the technical characterization of rubbers. If f is the load at an extension ratio α, then for small extensions, a statistical theory gives[8]:

$$f = \rho_r \frac{RT}{M_c}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{2}$$

In Figure 2, values of f, as measured on a Goodbrand testing machine, are plotted against $10^4/M_c$ for all the compounds employed in the experimental part of this investigation. While the results are seen to diverge widely from the form of Equation (2), except at small degrees of cross-linking, they are all satisfactorily represented by a single empirical curve. In the absence of any other data, it is suggested, therefore, that these curves may be employed to estimate the degree of cross-linking of a pure-gum vulcanizate when the load at an extension of 300 or 500 per cent is known. This method has not been sufficiently widely tested to make possible an estimate of its reliability. It must be regarded as only approximate, and the two curves do not necessarily give exactly the same degree of cross-linking for a particular rubber.

Curve 1 of Figure 3 gives a plot of the dependence of degree of cross-linking, estimated from the extension produced in a swollen specimen by a small load,

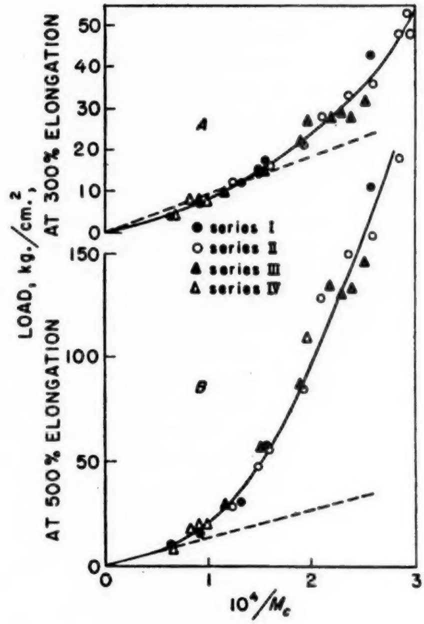

FIG. 2.—Dependence of load at (A) 300% elongation, (B) 500% elongation, on cross-linking; broken lines calculated from Equation (2).

on the sulfur content of a series of rubber-sulfur compounds, vulcanized at 142° C. These were prepared in various ways, using either crepe or acetone-extracted crepe, cured *in vacuo*, in open steam, or press-cured. All the points lie on a single line, indicating that the number of cross-links introduced is proportional to the amount of sulfur combined.

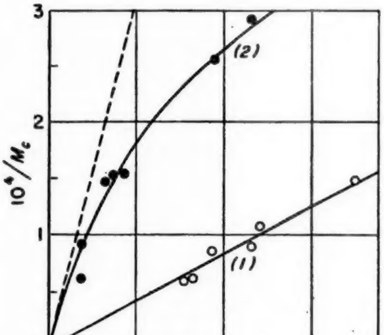

FIG. 3.—Dependence of cross-linking on combined sulfur: (1) unaccelerated compounds; (2) series I; broken line calculated for monosulfide links.

Four series of accelerated compounds have been made up, employing various accelerators, in which a systematic variation of cross-linking has been introduced by changing either the composition or the time and(or) temperature of cure. The degree of cross-linking was estimated as previously described and compared with the combined sulfur. The data for series I are shown in curve 2 of Figure 3, and a very marked difference from curve 1 is evident. The cross-linking efficiency is much higher, but tends to fall as more sulfur combines. Series II and III give curves very similar to curve 2, but series IV is widely different again. It will be seen from the analytical data that in these compounds, a moderate degree of cross-linking has been achieved without the combination of any measurable quantity of sulfur. The cross-linking efficiencies of a series of different accelerators have not yet been examined systematically, but it is already clear that wide variations exist and that, for a given accelerator, the efficiency depends both on the composition of the compound and on the vulcanization temperature.

The dotted line in Figure 3 gives the theoretical relationship between $10^4/M_c$ and the amount of combined sulfur, assuming every sulfur atom to form a monosulfide link. This is clearly the maximum possible efficiency of cross-linking by sulfur, and the chemical evidence[9] suggests that the true efficiency may be smaller. The agreement as to the order of magnitude between theory and experiment must be considered very satisfactory, as the basis on which $10^4/M_c$ has been estimated does not encourage the belief that this figure is exact in an absolute sense. It appears certain that the rubbers of Series IV must be vulcanized by direct C—C cross-links; this is in agreement with Farmer's discussion of the mode of action of tetramethylthiuram disulfide[10], the accelerator employed in this series.

TENSILE STRENGTH AND CROSS-LINKING

The literature contains many data on the effect of combined sulfur content on tensile strength. Some of these are presented in Figure 4 and show the characteristic feature of a well-defined maximum; beyond a certain critical sulfur content, the tensile strength falls very sharply. In the region of this

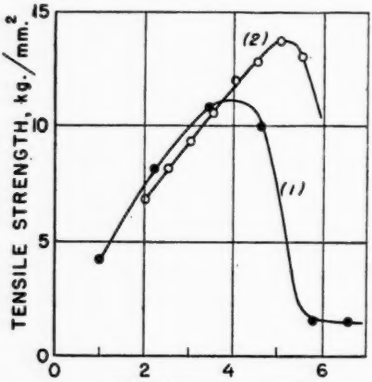

FIG. 4.—Effect of combined sulfur on tensile strength of rubber-sulfur mixes (92.5:7.5) cured at 148°: curve (1), ref. 11; curve (2), ref. 19.

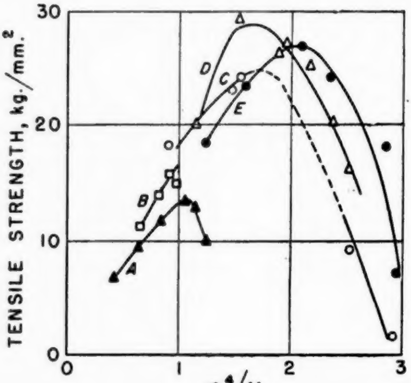

FIG. 5.—Effect of cross-linking on tensile strength: (A) unaccelerated[19]; (B) series IV; (C) series I; (D) series III; (E) series II.

critical composition, tensile data tend to be irreproducible, samples cut from a single sheet giving, at times, widely different strengths and extensibilities. The critical sulfur content is close to 5 per cent, though there is some evidence that it may depend slightly on the initial sulfur content of the mix, and perhaps also on the conditions of vulcanization.

Series I*

Zinc Diethyldithiocarbamate Compounds

Z.D.C., %	Sulfur		$10^4/M_c$	Load (kg. per sq. cm.)			Elongation (%)	Tensile strength (kg. per sq. mm.)
	Initial	Combined		300%	500%	Break		
0.5	1	0.75	0.91	7.5	$15._5$	186	890	18.4
0.5	4	1.3	1.47	$14._5$	48	274	755	23.4
0.5	7	1.7	1.54	$17._5$	52	291	745	24.5
1.0	4	3.8	2.5_5	43	183	156	470	8.9
1.0	7	4.6	2.9			47	270	1.7

* Each compound contained: rubber 100, zinc oxide 2, stearic acid 0.5, Nonox 0.5, and was vulcanized one hour at 100° C.

Series II*

Cure		Combined sulfur	$10^{14}/M_c$	Load (kg. per sq. cm.)			Elongation (%)	Tensile strength (kg. per sq. mm.)
Min.	° C			300%	500%	Break		
30	100	1.5_5	1.23	12	29	209	800	18.7
60	100	1.5_5	1.59	16	56	288	755	24.7
5	142	2.3_5	1.92	21	85	326	730	27.0
120	100	2.8	2.09	28	129	346	690	27.3
180	100	2.7	2.35	33	150	323	660	24.5
15	142	3.4	2.84	48	197	273	570	18.3
30	142	4.3	2.95	48		137	435	7.3

* Each compound contained: rubber 100, zinc oxide 5, stearic acid 1, Nonox 1, sulfur 4, diphenylguanidine 1, mercaptobenzothiazole 0.5.

Series III*

Cure		Combined sulfur	$10^4/M_c$	Load (kg. per sq. cm.)			Elongation (%)	Tensile strength (kg. per sq. mm.)
Min.	° C			300%	500%	Break		
30	100	0.3_5	1.16	10	30	223	810	20.3
60	100	1.4_5	1.53	15	57	337	790	30.0
5	142	$1._5$	1.89	22	87	327	725	26.9
120	100	1.8_5	1.96	27	110	341	705	27.4
180	100	2.1_5	2.17	28	135	334	670	25.8
15	142	2.1_5	2.38	28	134	282	630	20.6
30	142	2.6	2.51	32	146	255	595	17.6

* Similar to series II, but with sulfur 3 instead of 4.

Series IV*

Tetramethylthiuram Disulfide Compounds

Cure		Combined sulfur	$10^4/M_c$	Load (kg. per sq. cm.)			Elongation (%)	Tensile strength (kg. per sq. mm.)
Min.	° C			300%	500%	Break		
5	142	>0.08	0.65_5	4	9	110	945	11.5
10	142	>0.06	0.82_5	8	17	152	840	14.2
20	142	>0.05	0.92	8	20	176	820	16.1
30	142	>0.07	0.97_5	8	20	172	793	15.3

* Each compound contained: rubber 100, zinc oxide 2, Nonox 1, T.M.T. 3.

Tensile strengths of the four series of accelerated compounds were determined on a Goodbrand testing machine, using dumbbell test-pieces. The results are tabulated below, while in Figure 5 the tensile strengths are plotted against the degree of cross-linking, with the addition of data for rubber + sulfur, obtained by combining Figures 3 and 4. Each series of compounds gives a somewhat similar curve, but the height and position of the maximum of the curve for rubber and sulfur differ considerably from those of the accelerated compounds. It is to be noted that all the curves converge closely toward a common line for sufficiently small degrees of cross-linking. If combined sulfur is plotted as abscissa, this regularity is entirely lost, and there is no evidence that the position of the maximum is determined by the sulfur content.

EFFECT OF SWELLING ON TENSILE STRENGTH

The effect on tensile strength of swelling the rubber in a liquid was investigated, using the four series of accelerated compounds. Dumbbells were im-

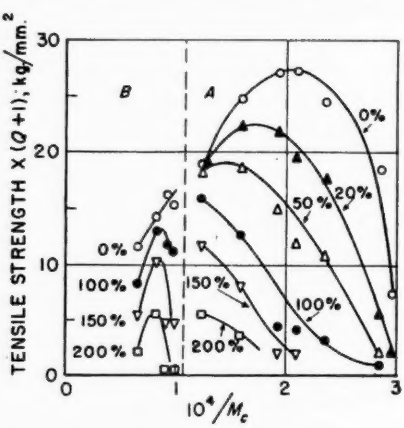

FIG. 6.—Effect of cross-linking on tensile strength of swollen rubbers: (A) series II; (B) series IV. Figures on curves give volume per cent of oil absorbed.

mersed in a commercial hydrocarbon oil of low vapor pressure (a light spindle oil) for various lengths of time. To equalize the distribution of the oil through the dumbbell, the swollen specimen was then heated overnight at 70° C in a closed tube in nitrogen. The tensile strengths, determined as above, were surprisingly reproducible, and were interpolated graphically to give the values at selected degrees of swelling. The data for a series of rubbers at the same oil content were then plotted as a function of the degree of cross-linking. Some of the results are shown in Figure 6, in which the ordinates represent tensile strength multiplied by the swelling ratio, *i.e.*, the ratio of the volumes of the swollen and dry rubbers. If l_0 and A_0 are the initial length and cross-section (dry), and l and W are the length and load at break when 1 cc. of rubber has imbibed Q cc. of liquid, the cross-section at break is $(Q + 1) \times A_0 l_0 / l$ and the tensile strength $Wl/l_0 A_0(Q + 1)$. The quantity plotted in Figure 6 is $Wl/l_0 A_0$; the object in doing this is to correct the data for the reduction of tensile strength by dilution.

Considering first Figure 6A, it is seen that for lightly cross-linked rubbers of series II the loss of tensile strength at small degrees of swelling is due entirely

to dilution, whereas highly cross-linked rubbers lose their strength much more rapidly on swelling. The data for rubbers of series I and III are essentially very similar, but the effect of swelling on the highly cross-linked samples is somewhat greater, and the progressive displacement of the maximum toward the left is not so striking. Figure 6*B* shows a qualitatively similar behavior in rubbers of series IV. All the rubbers of this series are only lightly cross-linked, and it is to be noted that a very high degree of swelling is needed to reduce the tensile strength by much more than is accounted for by the dilution.

EFFECT OF TEMPERATURE ON TENSILE STRENGTH

A systematic investigation of the tensile strengths of several natural rubber compounds over a wide range of temperatures was carried out by Tener, Kingsbury, and Holt[2], some of whose data are reproduced in Figure 7. In general the tensile strength rises rapidly from its low value in the brittle state to a maximum in the vicinity of $-50°$ C. Further rise in temperature then

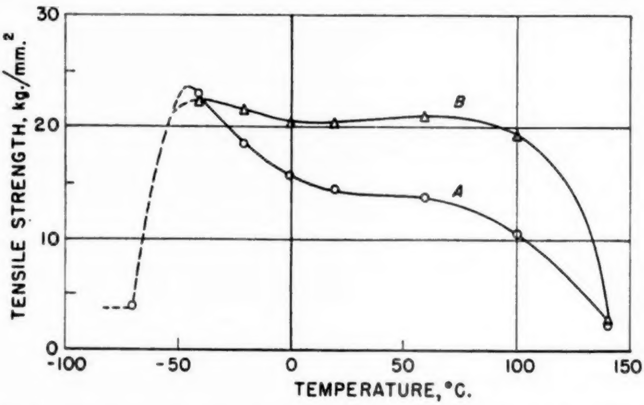

FIG. 7.—Effect of temperature on tensile strength[1]: (*A*) unaccelerated 8% sulfur; (*B*) tetramethylthiuram disulfide accelerated 1.9% sulfur.

produces relatively small changes of tensile strength until, in the neighborhood of 100° C, the strength falls rather sharply to a very low value. Other workers have shown that the shape of the curve between 0° and 100° C is highly dependent on the compound, even in pure-gum mixes. The *Vanderbilt News*[11] records test data at 25° and 100° C for a series of eleven pure-gum compounds at various states of cure. In most of these, the lightly cured specimens are some 50 per cent stronger at 100° than at 25° C. The effect of increasing time of cure is complicated by the fact that most of these compounds show reversion, *i.e.*, the load at a given elongation (300 or 500 per cent) passes through a maximum and diminishes again. According to Figure 2 this implies a maximum degree of cross-linking, followed by a reduction. In Figure 8 some representative data are plotted in such a way as to bring out the effect of reversion, the arrows on the curves representing the direction of increasing time of cure. Figure 8*A* refers to a compound containing a relatively high proportion of sulfur, and it will be seen that at the longest cures the tensile strength at 100° C diminishes very rapidly, and falls much below the value at 25°. No such behavior is found in Figure 8*B*, which refers to a compound of very low sulfur content.

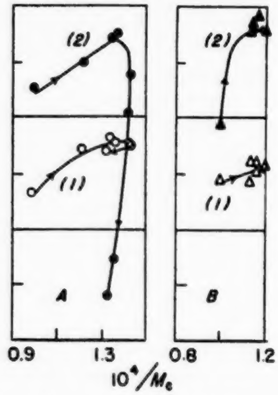

FIG. 8.—Effect of prolonged cure on tensile strength of two pure gum compounds. (A) high, (B) low sulfur, at 20° C (curves 1) and 100° C (curves 2). Arrows indicate direction of increasing cure.

Van Rossem and van der Meijden[12] measured the tensile strengths of simple rubber-sulfur compounds over the temperature range 20° to 150° C and found, in general, a curve showing a maximum strength at some intermediate temperature. The temperature beyond which the tensile strength began to fall rapidly was diminished by an increase in the percentage of combined sulfur.

No comprehensive study of the effect of temperatures has yet been undertaken in these laboratories, but preliminary data demonstrate very clearly that highly cross-linked compounds lose their tensile strength on heating much more rapidly than do more lightly cured compounds from the same stock.

DISCUSSION

The evidence summarized above shows clearly that the tensile strength of a pure-gum natural rubber compound is a function of many variables, among which the following appear especially important: (1) the degree of cross-linking,

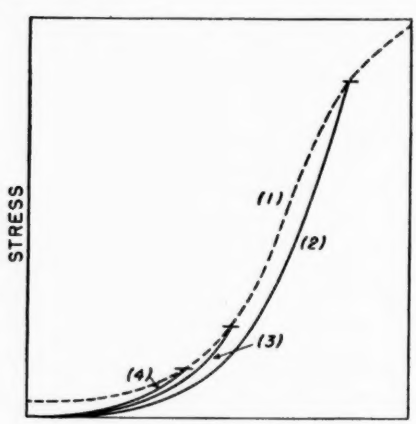

FIG. 9.—Schematic explanation of low tensile strength of highly cross-linked rubbers: (1) ultimate strength as a function of elongation; (2), (3), and (4) stress-strain curves of three rubbers.

(2) the type of compound, and (3) the temperature of test. It is now proposed to outline a suggested qualitative explanation of the effects of these factors, based on the assumption that the strength of rubber depends very markedly on the degree of crystallization. If a test-piece is broken under conditions such that crystallization is absent, a very low result ($\sim$1 kg. per sq. mm.) is obtained; the higher the degree of crystallization at break, the greater the tensile strength.

Let us consider first the effect of cross-linking in a series of compounds of similar composition, *e.g.*, a rubber-sulfur mixture cured for various lengths of time. The uncured material is weak because it is so plastic that elongation does not cause sufficient molecular alignment to induce crystallization. The introduction of a few cross-links suppresses plastic flow and thus makes crystallization possible. This effect is believed to be the origin of the rise of tensile strength with small degrees of cross-linking shown by the curves of Figure 5. It is important to emphasize that the cross-links are only necessary because the raw material is plastic. If unmasticated rubber is stretched rapidly, especially at a slightly reduced temperature, it crystallizes well and is very strong. Indeed, Rosbaud and Schmid[13] have reported a tensile strength of 42 kg. per sq. mm. for smooth smoked sheet at $-20°$ C.

The fall of tensile strength at high degrees of cross-linking can be understood by reference to the schematic diagram of Figure 9. Curve 1 (broken line) indicates the ultimate strength of the rubber, low at first, but increasing rapidly as the rubber crystallizes on extension. This curve represents the strength which the material would have if it could be tested at a range of elongations. It is assumed for the moment that this curve is the same for the three rubbers whose stress-strain curves are represented by Curves 2, 3, and 4. As a rubber strip is extended, the load tending to cause rupture increases, but at the same time crystallization causes the material to become stronger. Rupture clearly occurs when the first effect overtakes the second; this is represented in Figure 9 by the intersection of the stress-strain curve with the curve of ultimate strength. It is evident that if the degree of cross-linking becomes sufficiently high, the modulus of elasticity is so large that the rubber breaks without crystallizing, as shown in Curve 4. It is consistent with this explanation that highly cross-linked rubbers of low tensile strength do in fact break at small elongations.

This discussion of the behavior of rubbers of very low and very high degrees of cross-linking accounts in a general way for the existence of an optimum degree of cross-linking. A more detailed study requires an examination of the effects of elongation and cross-linking on the degree of crystallization at a given extension, since on this depend the shape and position of curve 1 of Figure 9. The form of this curve is at present quite uncertain. Not only is the exact dependence of tensile strength on degree of crystallization unknown, but different estimates of the degree of crystallization are rather divergent.

The effect of crystallization on the form of the stress-strain curve is complex. The slow crystallization of a strip of rubber held at constant length is accompanied by a decrease of tension[14]. On the other hand, the formation of crystallites at an early stage of the elongation has a reinforcing influence on the amorphous rubber, increasing the modulus of elasticity and reducing the extensibility. This leads to an apparent anomaly in the relative positions of the stress-strain curves measured at two different temperatures, say 20° and 100° C. At 20°, crystallization commences at a much smaller elongation than at 100°, and the 20° curve is generally found to lie almost wholly above the 100° curve.

Nevertheless, if the rubber is cooled at constant length, from 100° to 20° there is in general a decrease of tension, in accordance with the well-known thermoelastic behavior of rubber[15]. Flory[3] has used the load at 500 per cent elongation as a relative measure of the degree of crystallization, but it is clear that this method is of limited validity.

Two x-ray studies of the problem have led to quantitatively different conclusions. Field[16] examined a number of pure-gum compounds, and concluded that crystallization approached a limit of the order of 80 per cent at intermediate elongations (500 to 600 per cent) and thereafter increased only slightly with further extension; this would suggest that the upper part of curve 1 would be more nearly horizontal. Moppel[17] has reëxamined the problem, and concludes that Field's estimates of the degree of crystallization at elongations up to 500 per cent are too large by a factor of about two. Furthermore, there is evidence that the volume change on stretching continues to increase quite continuously to the vicinity of the breaking elongation[18]. The balance of evidence thus seems to suggest that crystallization increases continuously with elongation right up to the breaking point.

The effect of cross-linking on the degree of crystallization at a given elongation is not very clear. Increase of cross-linking would, in the absence of crystallization, reduce the extensibility and thus lead to greater alignment at high elongations. In general, however, crystallization commences at relatively small elongations, where this effect would not be important. Once crystallization has started, its reinforcing action modifies profoundly the elastic behavior of the rubber, as has already been noted. Field's *x*-ray data show two opposite tendencies. Considering any particular compound, increase in the time of vulcanization produces first a rapid rise, then a slow fall, in the degree of crystallization at 600 per cent elongation. During this second part of the curve, the load at 500 per cent elongation is, in most cases, still increasing slightly. On the other hand, if comparison is made among a series of different compounds, each of which has received a normal period of vulcanization, the crystallization at 600 per cent elongation shows a general tendency to increase slightly with the load at 500 per cent elongation. The first of these two observations will be discussed below, in the section on "overcure, reversion, and aging"; the second suggests a small increase in crystallization with increased cross-linking. Its effect is, of course, to displace curve 1 of Figure 9 to the left with increasing cross-linking, and thus extend the range of cure consistent with high tensile strength.

This argument is readily extended to permit a discussion of the effects of temperature and swelling. Apart from the dilution effect of an added liquid, which has been allowed for in presenting the experimental results, it is to be anticipated that swelling would have a somewhat similar effect to rise of temperature. At a given elongation, either factor clearly reduces the amount of crystallization, and thus tends to diminish the tensile strength. It is reasonable to expect the diminution to be most marked for highly cross-lined compounds, for it is clear from Figure 9 that a displacement of the rising portion of Curve 1 toward higher elongations would diminish the critical upper limit of cross-linking consistent with high tensile strength. Figure 6 and the preliminary study of the effect of temperature confirm this prediction; retention of high tensile strength at high temperatures or during swelling being confined to lightly cross-linked materials.

It is at first sight contrary to the above argument that certain compounds have been found to be stronger at 100° C than at room temperature (compare

especially Figure 8). It is to be noted that in these cases the extensibility increases very markedly with rise of temperature, typical figures being 800 per cent at 25° C, and 1100 per cent at 100°. The probable explanation of this is that the higher temperature delays the onset of crystallization and thus makes it possible for the chains to align more efficiently on stretching. Hence, although at a given elongation the degree of crystallization is diminished by rise of temperature, it is possible that the ultimate degree of crystallization attainable before breaking may actually increase with rise of temperature over a certain range. This is certainly the case for rubbers in the temperature range −70° to −50° C; the evidence suggests that there may be a second such range between 20° and 100° C for lightly cross-linked rubbers.

So far it has been tacitly assumed that a vulcanizate can be adequately characterized by its degree of cross-linking. It is clear from Figures 5 and 6 that this is not the case, and that the composition of the compound plays an important role. Comparing a series of rubber–sulfur compounds with accelerated compounds (Figure 5) the former cannot be nearly as highly cross-linked as the latter without becoming weak. The small effect of swelling agents or of inert fillers makes it fairly certain that this difference is not due to the presence of uncombined sulfur. Figure 3 shows that unaccelerated compounds contain relatively much larger amounts of combined sulfur. Farmer and his coworkers[9] have shown that much of this is in the form of small rings, formed by the linking together of two consecutive residues of a single chain by a sulfur atom. It is evident that these rings, randomly disposed along the chains, offer most effective opposition to crystallization. The effect is to lower curve 1 of Figure 9 and thus reduce the upper limit of cross-linking consistent with high tensile strength.

Vulcanization by sulfur thus involves a compromise between the desired feature of cross-linking and the undesired feature of structural irregularities introduced by sulfur combination. Optimum tensile strength should, therefore, be found in compounds which give the highest degree of cross-linking for a given sulfur content. Figure 6*B* shows that this conclusion is invalid for compounds vulcanized with T.M.T. (tetramethylthiuram disulfide) without added sulfur. It has been suggested above that these are vulcanized by direct C—C cross-links, which would seem at first sight to be an ideal method of vulcanization, introducing cross-links without other chemical modification of the rubber. The work of Bolland and Orr[19] on the thermal degradation of rubber shows that, once free radicals are produced, a variety of reactions becomes possible, and it is clearly unsafe to assume that vulcanization by T.M.T. involves no side reactions. The weakness of some of these compounds when highly swollen suggests that structural modifications, possibly cyclization, do indeed occur.

OVERCURE, REVERSION, AND AGING

A great deal of further work is needed to enable the foregoing discussion to be placed on a satisfactory quantitative basis. The factors affecting crystallization are complex and imperfectly understood. At the same time, there seems to be little doubt of the essential relation between tensile strength and crystallizability. It is, therefore, worth while to consider briefly the bearing of the ideas which have been set out on three phenomena of considerable interest and technical importance, namely, overcure, reversion, and aging.

If a given mix is heated at vulcanization temperature, the tensile strength is frequently found to pass through a maximum, and to diminish again on further

heating; this reduction of tensile strength is generally termed *overcure*. It is clear that this may occur because a very high degree of cross-linking has been produced, but it occurs also in certain cases where the final degree of cross-linking is small. A typical example is furnished by a mix[20] containing sulfur 3.5, zinc oxide 5, and M.B.T. 1, per 100 parts of rubber. After 15 minutes at 141° C, $10^4/M_c$ was 1.24 (estimated by means of Figure 2 from the load at 500 per cent elongation) and the tensile strength was 18.9 kg. per sq. mm. Further heating produced a steady fall of tensile strength (to 13.7 kg. per sq. mm.) without change of cross-linking. The probable explanation of this fall is that sulfur combination continues throughout the heating period, although the degree of cross-linking reaches a limit. This is probably the explanation of Field's observation, noted above, that the crystallinity of a compound usually passes through a maximum and diminishes again on prolonged vulcanization.

In some compounds the load at 500 per cent elongation is found to pass through a maximum on prolonged heating, and the rubber is then said to revert. Nothing which has been put forward above offers any physical explanation of this phenomenon. Indeed, if we accept the evidence of Figure 2 of a unique relationship between load and cross-linking, it is obvious that reversion can only be explained by a chemical reaction or reactions involving a net decrease in the number of cross-links. This could arise either from chemical instability of the cross-links or from a concurrent scission process.

There is widespread acceptance of the view that the gradual loss of tensile strength aging is the result of oxidative scission. It is certainly true both that rubber can undergo oxidative degradation, and that aging is greatly retarded if oxygen is excluded, but an examination of the changes of modulus and tensile strength during aging suggests that the simple chemical theory is inadequate. We may imagine that the chemical reactions occurring during aging are divided into two classes, according to whether they modify the degree of cross-linking or produce other structural changes likely to influence crystallization. The scission theory in its simplest form would neglect the second factor, and suppose aging to consist essentially in a reduction in the degree of cross-linking. The effect of this on the tensile strength can be seen at once from Figure 5. A lightly cross-linked material would lose its strength continuously; a highly cross-linked one would become first stronger and then weaker. General experience is directly opposed to these expectations, overcured compounds being characterized by their very bad aging properties[20]. A survey of the effect of Geer oven aging at 70° C on the tensile properties of a number of pure-gum compounds reveals no direct connection between cross-linking changes during aging and tensile strength. In many cases the net degree of cross-linking, as estimated from the load at 500 per cent elongation, appears to increase during aging. Tobolsky and Andrews[21] have advanced evidence that both cross-linking and scission processes occur during heat aging. It now appears that the second type of chemical reaction, involving structural changes which interfere with crystallization, is also of great importance, since in some cases a very serious loss of tensile strength may occur without appreciable change in the net degree of cross-linking.

The problems raised in this final section can of course only be solved by chemical investigation. The purpose of introducing them in this paper was simply to call attention to them, and no useful purpose would be served by speculating as to the possible chemical reactions involved.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance in this work given by a number of his colleagues. His thanks are especially due to S. C. Stokes for the preparation of the rubber compounds, to T. A. Sharpley for the tensile test data, and to W. T. Chambers for the analyses. This paper forms part of the program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

SUMMARY

The tensile properties of a range of pure-gum natural rubbers have been reviewed, and it has been shown that their principal features can be understood on the assumption that the tensile strength measured in a given test depends directly on the amount of crystallization at break. The most important single factor in determining tensile strength is the degree of cross-linking. Cross-linking is only needed in order to prevent plastic flow, thus making it possible for the molecules to align themselves by stretching, and hence to crystallize. A very highly cross-linked rubber is weak because the load required to stretch it is so high that the rubber is broken before the elongation becomes large enough to produce crystallization. In general, vulcanization also involves reactions, *e.g.*, the combination of sulfur with the rubber, which inhibit crystallization by producing structural modifications of the rubber. These reduce the tensile strength, especially when the degree of cross-linking is large. These ideas readily explain the effects of swelling and of the temperature of test. They are also used in a brief discussion of the phenomena of overcure, reversion, and aging.

REFERENCES

[1] Throughout this paper, we shall depart from the custom of the rubber industry, and express all tensile strength values on the actual cross-section at break. This value is sometimes called by rubber technologists the "tensile product".
[2] Tener, Kingsbury and Holt, U. S. Bur. Standards, Tech. Paper No. **364** (1928).
[3] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[4] Gee, "General Discussion on Swelling and Shrinkage", presented before the Faraday Society, Sept. **1946**.
[5] Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
[6] Boyer and Spencer, paper presented before the High Polymer Division, Am. Physical Society, Jan. **1946**.
[7] Gee and Orr, *Trans. Faraday Soc.* **42**, 507 (1946).
[8] Wall, *J. Chem. Physics* **10**, 485 (1942).
[9] Farmer *et al.*, *J. Polymer Science* **1**, 293, 305, 312 (1946).
[10] Farmer, *Trans. Faraday Soc.* **38**, 356 (1942).
[11] *Vanderbilt News* **4**, No. 4 (1934).
[12] Van Rossem and van der Meijden, *J. Soc. Chem. Ind.* **45**, 67T (1926).
[13] Rosbaud and Schmid, *Z. techn. Physik* **9**, 98 (1928).
[14] Alfrey and Mark, RUBBER CHEM. TECH. **14**, 525 (1941).
[15] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935).
[16] Field, *J. Applied Physics* **12**, 23 (1941).
[17] Goppel, Thesis, Delft, **1946**. See also Wildschut, "Technological and Physical Investigations on Natural and Synthetic Rubbers", Elsevier Publishing Co., New York and Amsterdam, **1946**, p. 156.
[18] Holt and McPherson, *J. Research Natl. Bur. Standards* **17**, 656 (1936); Treloar, *Trans. Faraday Soc.* **37**, 84 (1941).
[19] Bolland and Orr, *Trans. Inst. Rubber Ind.* **21**, 133 (1946).
[20] Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assocn. Brit. Rubber Manufrs., Croydon, **1935**.
[21] Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945).

THE THERMOELASTIC PROPERTIES OF RUBBER *

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INTRODUCTION

In an earlier communication[1] it was shown that, within a certain range of elongations, *viz.*, 100 to 300 per cent, and at constant elongation, the stress in stretched rubber is directly proportional to the absolute temperature. Within this range, therefore, the stress is analogous to the pressure of an ideal gas, which at constant volume is likewise proportional to the temperature. This behavior of rubber and of other rubberlike substances is said to be *ideal.*

However, a sample of rubber the behavior of which is ideal at elongations of 100 per cent and higher deviates from this behavior when its elongation is less than 100 per cent or greater than 500 per cent. One of the reasons for these deviations from ideal behavior at high deformations has already been discussed in a previous publication[2]; as a result of stretching, rubber begins to crystallize. The crystallites do not contribute to the elastic force, but if the temperature is raised, they fuse and thereby increase the stress, which then increases more rapidly than that of an ideal rubber.

The deviations from ideal behavior at small deformations have not in any way been studied thoroughly, so the first part of the present work is concerned with these deviations from ideal behavior. First of all it is well to discuss some experimental facts. The thermal coefficient of the force F at constant elongation Δl, $(\partial F/\partial T)_{\Delta l}$, is negative for low elongations (up to about 10 per cent), *i.e.*, the force decreases with rise in temperature, and the coefficient of linear expansion in the direction of traction remains positive, like that of an ordinary material. At elongations of approximately 10 per cent, the stress is independent of the temperature; at this point the coefficient of linear expansion in the direction of stretching is, therefore, equal to zero. At higher deformations, the stress increases with rise in temperature, a phenomenon which indicates a negative coefficient of linear expansion.

On the other hand, if rubber is deformed in the opposite sense to elongation, *i.e.*, by exerting a pressure in only one direction, the coefficient of linear expansion:

$$\left(\frac{\partial l}{\partial T}\right)_F$$

remains at all times positive. The pressure exerted by the rubber against this force increases very rapidly at first with rise in temperature when the deformation is small. At higher deformations, the behavior of the rubber tends toward the ideal.

THERMODYNAMICS OF ISOTHERMAL DEFORMATIONS

To interpret these phenomena on a molecular basis, the thermodynamic equations of isothermal deformations must first of all be established. Up to

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the present time, any changes in volume during elastic deformation have been disregarded, and materials have been treated as if they were incompressible[3]. However, unilateral compression certainly involves an increase in pressure, at least at certain points in the sample, whereas a tractive force has the opposite effect. An increase in pressure results in a decrease in volume and, conversely, the volume is increased by traction, and the more compressible the material, the greater is this increase in volume.

It can be readily shown that, when stretched, rubber tends to increase in volume. A cylindrical tube of vulcanized rubber, placed horizontally, is filled with water; it is then closed at one end and a glass capillary tube is inserted into the other end. When the rubber tube is stretched, the water is withdrawn further into the capillary, *i.e.*, the internal volume of the rubber tube is increased by the stretching[4]. If the water inside the tube is replaced by rubber, the volume of the latter must likewise increase, although to a much less degree. This phenomenon will be taken into account in the following discussion.

A part of the work expended in stretching rubber is, therefore, absorbed as work of change in volume against the external pressure, *e.g.*, against atmospheric pressure. If at constant temperature T and constant pressure P, a sample of rubber is deformed (elongated), the infinitesimal distance dl, the work expended on the rubber is $F \cdot dl$. This work is equal to the sum of the changes in energy and of the product $-TS$ (where S is the entropy), plus the work of change in volume against the pressure, $P \cdot dV$:

$$F \cdot dl = dE - T \cdot dS + P \cdot dV \tag{1}$$

Since this involves a transformation at constant temperature and constant pressure, it is possible to write:

$$F = \left(\frac{\partial E}{\partial l}\right)_{T,P} - T\left(\frac{\partial S}{\partial l}\right)_{T,P} + P\left(\frac{\partial V}{\partial l}\right)_{T,P} \tag{2}$$

With the length l and the pressure P maintained constant, the derivative with respect to T is:

$$\left(\frac{\partial F}{\partial T}\right)_{l,P} = \left[\frac{\partial^2 E}{\partial T \cdot \partial l} - T\frac{\partial^2 S}{\partial T \cdot \partial l}\right] - \frac{\partial S}{\partial l} + P\frac{\partial^2 V}{\partial T \cdot \partial l} \tag{3}$$

The term within the brackets can be written:

$$\frac{\partial}{\partial l}\left[\frac{\partial E}{\partial T} - T\frac{\partial S}{\partial T}\right] \tag{3a}$$

If l and P are constants, $dl = 0$ and $dP = 0$, and thus Equation (1) becomes:

$$0 = dE - T \cdot dS + P \cdot dV$$

from which, with l and P constant, the following equation is derived:

$$\left(\frac{\partial E}{\partial T}\right)_{l,P} - T\left(\frac{\partial S}{\partial T}\right)_{l,P} + P\left(\frac{\partial V}{\partial T}\right)_{l,P} = 0$$

The term within the brackets in Equation (3a) reduces itself to:

$$-\frac{\partial}{\partial l}P\frac{\partial V}{\partial T} = -P\frac{\partial^2 V}{\partial l \cdot \partial T} \tag{3b}$$

Hence Equation (3) becomes:

$$\left(\frac{\partial F}{\partial T}\right)_{l,P} = -\left(\frac{\partial S}{\partial l}\right)_{T,P} \tag{4}$$

By substituting in Equation (2) the expressions (3b) and (4), there is obtained:

$$F = \left(\frac{\partial E}{\partial T}\right)_{T,P} + T\left(\frac{\partial F}{\partial T}\right)_{l,P} + P\left(\frac{\partial V}{\partial l}\right)_{T,P} \tag{5}$$

In this way the equation obtained is the same as that of Elliott and Lippmann[5].

The authors point out that, at an infinitely small pressure, the equation reduces itself to that derived by Wiegand and Snyder[6], and, independently, by Meyer and Ferri[7]. This relation still holds true if $\partial V/\partial l = 0$, whatever the value of P, and this last approximation (the constancy of volume during isothermal deformation) was used in the calculations[8]. Within the scope of this approximate theory, a distinction between $(\partial E/\partial l)_{P,T}$ and $(\partial E/\partial l)_{V,T}$ is hardly possible[9]. The present authors are in accord with the other investigators in believing that the correction applied to the elastic force in the first work[7] is not really warranted, and one of the purposes of the present work is to eliminate this correction. No attempt will be made to discuss the other conclusions of Elliott and Lippmann, in particular their Equations (38) and (45), for which there does not appear to be any justification.

Let us now examine the numerical significance of the work of change in volume in relation to the work of elasticity. For rubber, the tensile modulus ϵ is approximately 10^7 dynes per sq. cm. The work required to stretch 1 cubic centimeter of rubber to twice its original length is, therefore, approximately 5×10^6 ergs. With the compressibility[10] of 5.1×10^{-11} sq. cm. per dyne, a decrease in the hydrostatic pressure of 10^7 dynes per sq. cm. increases the volume by 0.05 per cent. During a unilateral traction of 10^7 dynes per sq. cm., an increase of the order of one-third of this, *i.e.*, 0.02 per cent, would be expected. The work of change in volume against atmospheric pressure, *i.e.*, about 10^6 dynes per sq. cm., is then 2×10^2 ergs. We have, then, as the work expended, 5×10^6 ergs, of which the work of change in volume ($P = 10^6$) is 2×10^2 ergs.

Hence, at least at relative low pressures, the work of change in volume in relation to the total work can be neglected. This also holds true in the same way of the work of change in surface (resulting from the increase in surface) against the surface tension. This increase in surface is 0.66 sq. cm. and is therefore appreciable, but the surface tension is of the order of only several times ten ergs.

The equations used up to this time can, therefore, be regarded as approximations which are quite satisfactory from a practical point of view. However, even if the change in volume with respect to work can be disregarded, it can no longer be disregarded if it is desired to interpret the changes in internal energy or in entropy in terms of molecular statistics. Actually a very small isothermal change in the volume of rubber is accompanied by a considerable change in entropy and in internal energy. Scott[11] has determined the coefficient of cubic expansion: $1/V(\partial V/\partial T)$ of vulcanized rubber as 6.61×10^{-11} per degree, and its compressibility: $1/V(\partial V/\partial P)$ as -5.10×10^{-11} sq. cm. per dyne.

From the general relations:

$$-\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P : \left(\frac{\partial V}{\partial P}\right)_T \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T - P$$

there is obtained, for $T = 300°$ K and atmospheric pressure $P = 10^6$ dynes per sq. cm.:

$$\left(\frac{\partial S}{\partial V}\right)_T = 1.3 \times 10^7 \text{ ergs per cc.-degree, and}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = 3.9 \times 10^9 \text{ ergs per cc.}$$

According to this relation, the behavior of rubber differs very little from that of ordinary liquids. Coefficients of expansion and compression found in the literature, for example, give the values ($T = 300°$ K and $P = 10^6$ dynes per sq. cm.) see in Table 1.

TABLE 1

Liquid	$\left(\frac{\partial S}{\partial V}\right)_T$ in ergs per cc. per degree	$\left(\frac{\partial E}{\partial V}\right)_T$ in ergs per cc.
Benzene	1.65×10^7	490×10^7
Ether	1.33×10^7	400×10^7
Paraffin oil	1.24×10^7	370×10^7
Rubber	1.3×10^7	390×10^7

The change in E for an increase in volume of rubber of 0.02 per cent is, therefore, 0.8×10^6 ergs per cc., a value which is of almost the same order of magnitude as the work required to elongate the rubber 100 per cent. Even still smaller changes in volume, which can be measured only with difficulty, must therefore not be disregarded.

STATISTICAL THEORY

It has been shown that the behavior of rubber at ordinary elongations is almost ideal. This means that the internal energy does not change and that the free energy is practically equal to the product of the temperature and the change in entropy. The latter is a means of expressing the probability, which is decreased by deforming the rubber, because the segments of molecular chains arrange themselves in a more orderly way and, consequently, a less probable way.

Consider now small elongations. Unquestionably these also bring about a more orderly geometric arrangement of the segments. However, experiments have shown that, instead of decreasing, the entropy increases with slight stretching[12]. This increase in entropy can be attributed to the increase in volume brought about by stretching. The changes in entropy result from the superposition of two causes: (1) rearrangement of the segments, and (2) change in volume. When the elongation is low, the second factor is dominant and the entropy increases; when the elongation reaches about 10 per cent, the two factors compensate for each other, and there is no change in entropy. At still higher elongations, the first factor predominates, and brings about a decrease in entropy.

The change in volume is likewise manifest, when rubber undergoes unilateral compression. This latter deformation brings about a decrease in

volume. This results in turn in a decrease in entropy, which in this case is added to that which originates from the less irregular arrangement of the segments. When rubber undergoes unilateral compression its entropy must, therefore, decrease more rapidly than that of an incompressible rubberlike material. This conclusion is in harmony with experimentally observed facts.

In both compression and in stretching, the smaller the deformation, the greater is the masking effect of the change in volume on the effect of rearrangement of the segments.

DEFORMATION BY SHEARING

The influence of changes in volume is clearly shown by comparing the results described above with a type of deformation in which there is simultaneous extension and compression in such a way that the increase in volume resulting from extension compensates for the decrease in volume resulting from the compression. In this case the volume remains constant. This is true of rotary shearing, such as takes place in a rheometer (see Figure 1).

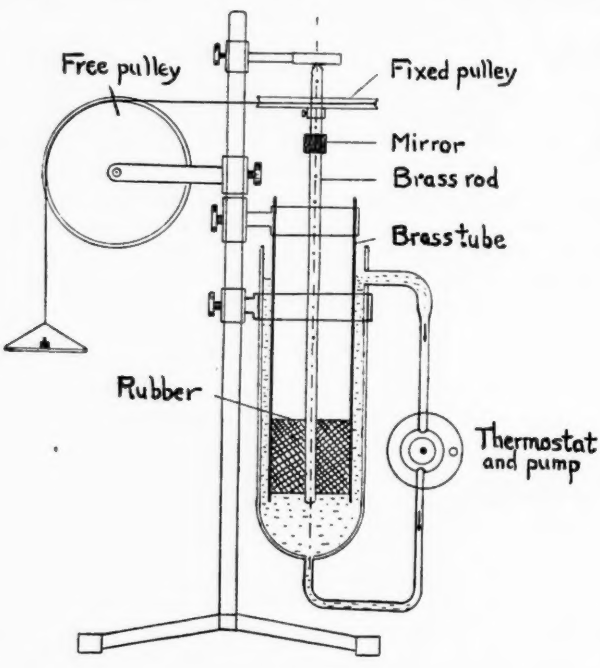

FIG. 1.

As shown in Figure 1, a cylinder of rubber is placed within a rigid brass tube with its entire lateral surface in contact with the brass tube. A cylindrical brass rod passes coaxially through the rubber. At the top of this rod are a small mirror and a pulley. A torsion couple is exerted by weights suspended on a wire which passes over a second freely rotating pulley connected by the wire to the first pulley, which is rigidly attached to the vertical rod. The torsion couple C is measured by the product of the weight supported by the

wire and the radius (35 mm.) of the fixed pulley. The torsion angle α is determined by means of a graduated scale, placed at 1 meter distance, and observed, after reflection in the mirror, through a magnifying glass.

The results of the measurements, the details of which will be described in the Experimental Part of the present paper, are reproduced in Table 2.

TABLE 2

COMPARISON OF THE VALUES OF $-T\partial S/\partial\alpha$ AT DIFFERENT TEMPERATURES WITH THOSE OF $\partial A/\partial\alpha$ IN ERGS PER DEGREE OF ANGLE FOR ONE GRAM OF RUBBER

Force (g.)	Couple (dynes per cm.)	$-10^{-3}T(\partial S/\partial\alpha)_T$						$10^{-3}(\partial A/\partial\alpha)_T$
		20°	30°	40°	50°	60°	70°	
45	1.55×10^5	—	13	13	14	12	12	12
95	3.26×10^5	27	25	26	26	26	26	25
145	4.98×10^5	48	47	39	38	37	37	38

$T/(\partial S/\partial\alpha)$ was calculated from the thermal coefficient of the couple; in this case very low values of this coefficient were chosen. Even for the largest couple, the angle of rotation was only two degrees. It is certain, therefore, that the measurements were made within the range of small dimensions, a range within which deviations from ideal behavior are particularly evident, provided that stretching is involved.

The last column of Table 1 gives the changes in free energy A with changes in the deformation $(\partial A/\partial\alpha)_T$ (calculated in the same units as those of the preceding columns of data). The numerical values refer to 1 gram of rubber. It is evident that the changes in free energy $\partial A/\partial\alpha$ are equal to those of $-T/\partial S/\partial\alpha$), and since, at constant temperature:

$$\frac{\partial A}{\partial\alpha} = \frac{\partial E}{\partial\alpha} - T\cdot\frac{\partial S}{\partial\alpha}$$

it follows that there is no change in internal energy. Accordingly rubber behaves in a practically ideal way even when only slightly deformed, provided that the deformation is shearing.

KINETIC THEORY

It has been shown that, for the particular type of deformation described, the effect of rearrangement is clearly defined. The elastic force originates solely from thermal movements of the segments, and no change in the forces of attraction are involved.

The considerable departure from ideal behavior at low elongations can, therefore, be explained by a very small increase in the volume of the rubber when it undergoes traction—an increase which escapes observation by ordinary experimental methods. This increase in volume takes place in the molecular plane through a slight displacement of groups of atoms, *e.g.*, of chain segments, which are displaced from their equilibrium position. This expansion results in an increase in internal energy. Now it is obvious that the greater this displacement from the equilibrium position, the greater is the resistance against the displacement. Furthermore, with increase in elongation, the chains orient themselves to a correspondingly greater degree in the direction of the force, and this acts to a progressively greater extent on the primary valences. However, the latter are so rigid that displacement of the atoms remains extremely small, and the increase in volume only slight. There is a second cause

of purely geometric origin, *viz.*, the decrease in the factor $(\partial V/\partial l)$ as l increases. The two causes cited act in the same sense, and account for the disappearance of the anomaly at mean elongations.

When crystallization takes place, *e.g.*, at elongations of 200 to 400 per cent, the entropy decreases (evolution of heat of crystallization) and the internal energy decreases to the same degree. When the point of rupture is approached, *i.e.*, at the moment when the chains are in a highly developed state of orientation, the internal energy again increases, for then the external force, having become relatively great, deforms the primary-valence angles, and this leads to an increase in energy and also an increase in entropy. On the other hand, compression results in decreases in energy and in entropy.

The trend of $\partial E/\partial l$ and of $\partial S/\partial l$ is, therefore, very complicated, because of the superposition of several factors, *viz.*, expansion against intermolecular forces of cohesion, elongation and orientation of chain molecules, possible crystallization and, finally, deformation of the primary-valence angles.

With respect to the first factor, it should be remembered that the forces of cohesion differ considerably, according to the chemical character of the rubberlike material. Compare, for example, the forces of cohesion in apolar elastic hydrocarbons with those in elastic ligaments, such as keratin from hair and collagen, which are much greater because of the presence of hydrogen bonds. It is, therefore, not surprising that the change in internal energy as a function of the degree of stretching is not the same for all rubberlike materials. For example, from a quantitative point of view, the butadiene-styrene copolymer, GR-S, behaves differently from natural rubber[13]. The behavior of hair is still more different from that of rubber, as has recently been shown by Woods[14]. However, the present authors believe that it would be wrong to draw the conclusion from these quantitative differences that the molecular phenomena which take place curing the stretching of hair differ qualitatively from those in rubber or in any other material possessing rubberlike elasticity. On the contrary, the present authors believe that the long range elasticity of keratins should not be attributed to a characteristic folding of the molecular chains under the influence of forces of attraction, as assumed by Astbury, but that the long range elasticity is of the same character as that of other materials with typical rubberlike properties.

EXPERIMENTAL PART

To analyze the thermoelastic behavior of a material, it is important to know the thermal coefficient of the deforming force when the degree of deformation is maintained constant. In the case of rotatory shearings, the deforming force acts as a couple C, and the deformation is measured by the angle of rotation α. The magnitude to be determined is, then, $(\partial C/\partial T)_\alpha$ for different deformations.

In virtue of the preceding equations:

$$-\left(\frac{\partial C}{\partial T}\right)_\alpha = \left(\frac{\partial S}{\partial \alpha}\right)_T$$

and assuming that rubber behaves in an ideal manner, it is necessary that

$$\left(\frac{\partial E}{\partial \alpha}\right)^T = 0$$

whence:

$$\left(\frac{\partial A}{\partial \alpha}\right)_T = \left(\frac{\partial E}{\partial \alpha}\right)_T - T\left(\frac{\partial S}{\partial \alpha}\right)_T = \left(\frac{\partial C}{\partial T}\right)_\alpha$$

where A is the free energy. The first member is in principle measurable directly. However, for various reasons, one of which is that it becomes difficult to carry out experiments at very small deformations, the present authors prefer a different procedure.

It can be shown that

$$\left(\frac{\partial C}{\partial T}\right)_\alpha = -\left(\frac{\partial C}{\partial \alpha}\right)_T \cdot \left(\frac{\partial \alpha}{\partial T}\right)_c$$

The first factor of the second member is proportional to the shearing modulus; it is therefore always positive. The second factor represents the change in deformation with temperature; it can, therefore, be positive as well as negative. Their product is equal to the derivative, $(\partial S/\partial \alpha)_T$.

The apparatus described and illustrated in the earlier part of this paper was used in the experiments now to be described.

Each of the two factors was measured seaparately. It is important that each pair of values thus obtained represents the same state of the rubber, and that this state represents a reversible transformation. It is, therefore, indispensable to avoid any effects such as plastic deformation and hysteresis. However, this is rather difficult to accomplish, for the relatively great thickness of the rubber sample prevents rapid exchange of heat. A thermometer, the bulb of which has the same diameter as that of the brass rod through the cylindrical rubber sample, and placed in the same position, indicated that thermal equilibrium does not become established until about 20 minutes after the temperature of the water is suddenly changed by 10 degrees. At least 45 minutes is necessary to be certain that the torsion angle does not vary and each measurement of $\partial \alpha/\partial T$, involving necessarily duplicate determinations, requires, therefore, a minimum of one and one-half hours. The method used for eliminating the influence of secondary effects was as follows.

The coefficient $(\partial \alpha/\partial T)_c$ was measured at 10-degree temperature intervals from 20° to 70° C in the following way. The rubber sample was maintained under the smallest tension at which measurable effects could be obtained, and at a temperature of 70° C until the torsion angle no longer varied appreciably during a period of two hours. The temperature was then raised to 75° C and held at this point for 45 minutes, then was held at 65° C for the same length of time, then at 75° C, and so forth. By noting each time the difference, $\alpha_{75} - \alpha_{65} = \Delta\alpha_{70}$, a series of data was obtained which represented an alternate rise and fall in temperature. The plastic deformation, which is to be subtracted in the first case and is to be added in the second case, tends to disappear in the mean of these $\overline{\Delta\alpha_{10}}$ values. This mean corresponds to temperatures 5° C above and 5° C lower than the mean temperature of 70° C, so $\Delta T = 10°$ C. Hence $(\overline{\Delta\alpha})/10$ should approach the value of $(\partial \alpha/\partial T)_c$ for the mean temperature of 70° C.

After this series of measurements, the temperature of the water was carried down to 60° C and maintained at this point until α did not vary during a period of 2 hours. From observations at 65° and at 55° C it was then possible to calculate $(\partial \alpha/\partial T)_c$ at the mean temperature of 60° C. In this way, all the $(\partial \alpha/\partial T)_c$ values were determined between 70° and 20° C for a load of 45 grams.

At the lowest temperature (15° C), the results were useless, for the rubber had become very sluggish.

In this first series of measurements, the tractive force was 45 grams, which corresponds to a couple of 1.55×10^5 dynes per cm. In a second series of observations, a load of 95 grams was used, so the corresponding values of $(\partial\alpha/\partial T)_c$ were for a couple of 3.26×10^5 dynes per cm. A third series was carried out with a load of 145 grams, corresponding to a couple of 4.98×10^5 dynes per cm. The results of these measurements are summarized in Table 3. All values should be multiplied by 10^{-3}

TABLE 3

VALUES OF $-(\partial\alpha/\partial T)_c$ IN DEGREES OF ANGLE PER DEGREE CENTIGRADE

Force (g.)	20°	30°	40°	50°	60°	70°
45	—	2.2	2.3	2.2	1.9	1.8
45	4.5	4.2	4.2	4.2	4.2	3.9
45	7.8	8.0	6.4	6.1	5.6	5.5

To determine $(\partial C/\partial\alpha)_T$, each series of measurements of $(\partial\alpha/\partial T)_c$ was interrupted in the middle, the temperature was carried to the mean value of the particular series, was held until equilibrium was established, and the load was then increased and decreased alternatively by 5 grams. The $\Delta\alpha$ values thus obtained correspond to a change in force of 10 grams, *i.e.*, $\Delta C = 3.43 \times 10^4$ dynes per cm. The value of the quotient $\Delta C/\Delta\alpha$ should be practically identical to that of $(\partial C/\partial\alpha)_T$ for rubber when the latter is in a state for which the corresponding $(\partial\alpha/\partial T)_c$ value has been measured. The results are recorded in Table 4. All results should be multiplied by 10^3.

TABLE 4

VALUES OF $\partial C/\partial\alpha$ IN DYNES PER CENTIMETER PER DEGREE OF ANGLE

Force (g.)	20°	30°	40°	50°	60°	70°
45	265	250	243	250	246	254
95	268	260	254	245	242	253
145	274	250	253	251	255	257

It is difficult to estimate the experimental errors. They are certainly greater for $\partial\alpha/\partial T$ than for $\partial C/\partial\alpha$, and relatively greater for small couples. It is believed, however, that in general the precision is of the order of ± 10 per cent for $\partial\alpha/\partial T$ and about 2 per cent for $\partial C/\partial\alpha$.

One source of error arises from possible slippage of the cylindrical rubber sample on the centre rod and on the tube. This slippage is inappreciable when degreased brass is used, and by heating the apparatus without tension for several days at 50–60° C, perfect adhesion between metal and rubber is obtained, without the necessity of attaching and thus deforming the rubber and without having to resort to an adhesive.

The rubber sample used for the tests was of the stopper type, prepared from the following mixture:

Rubber	100
Sulfur	3
Diphenylguanidine	1
Aldolnaphthylamine	2
Paraffin	3
Zinc oxide	5

It was made cylindrical by grinding with a coarse stone at slow speed so as to avoid excess heating locally.

By multiplying together the corresponding values in Tables 2 and 3, dividing the results by the weight of rubber (13 grams), and multiplying by T, the values recorded in Table 1 were obtained.

SHEARING AND STRETCHING

The data in Table 4 make it possible also to compare the deformations obtained by shearing with those obtained by stretching. The two types of deformation are geometrically dissimilar, and only the accumulated energy can be compared.

According to the data in Table 4, $\partial C/\partial \alpha$ was virtually constant at $\approx 2.55 \times 10^5$. The free energy of the rubber subjected to couple C was, therefore

$$\int C \cdot d\alpha = \int C \frac{dc}{2.55 \times 10^5} \approx \frac{10^{-5}}{5.1} C^2 \text{ ergs}$$

Since the weight of the sample was 13 grams, the free energy per gram of rubber was:

$$A_c = \frac{10^{-5}}{5.1 \times 13} C^2 \text{ ergs} \tag{6}$$

Let us then calculate what elongation corresponds to this free energy. For a cube 1 centimeter on a side (weighing virtually 1 gram), $A_l = f \cdot dl$.

It is known that the mean value of the tensile modulus is:

$$\epsilon = \frac{\partial f}{\partial l} \approx 1.4 \times 10^7$$

and is practically constant between 0 and 30 per cent elongation. If the elongation is designated by Δl, there results:

$$f = 1.4 \times 10^7 \Delta l$$

and

$$A_l = \int 1.4 \times 10^7 (\Delta l) dl = 0.7 \times 10^7 (\Delta l)^2 \tag{7}$$

If this energy is equal to that obtained by shearing, there results, according to Equations (6) and (7):

$$(\Delta l)^2 = \frac{10^{-5}}{5.1 \times 13} \cdot \frac{10^{-7}}{0.7} C_z$$

whence:

$$\Delta l = 1.47 \times 10^{-7} C$$

Thus the couples utilized in the experiments described correspond to the elongations shown in Table 5.

TABLE 5

Couple (dynes per cm.)	Elongation (percentage)
1.55×10^5	2.3
3.26×10^5	4.8
4.98×10^5	7.3

The couples chosen correspond in all cases to elongations lying between 0 and 10 per cent, *i.e.*, in the range where deviations from ideal behavior are especially pronounced.

RÉSUMÉ

Deviations from ideal behavior shown by rubberlike materials when subjected to small elongations or compressions arise from small changes in volume, which cause changes of considerable magnitude in the internal energy and entropy. On the contrary, ideal behavior is exhibited, even at very small deformations, by application of a shearing force, for the latter causes no change in volume.

SUPPLEMENTARY NOTE

A recent work by Gee[15] has just become available to the present authors. The increase in volume brought about by stretching is calculated by Gee in a different way. The result, 0.027 per cent at an elongation of 70 per cent was confirmed by direct measurements, which gave a mean value of 0.035 per cent at an elongation of 80 per cent. The estimate of the present authors, *viz.*, 0.02 per cent at 100 per cent elongation, is therefore of the same order of magnitude.

REFERENCES

[1] Meyer, von Susich and Valkò, *Kolloid-Z.* **59**, 208 (1932).
[2] Meyer and Ferri, *Helv. Chim. Acta* **28**, 570 (1935).
[3] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935); Meyer, "Die hochpolymeren Verbindungen", Akad. Verlags-Ges., Leipzig, **1940**, p. 139.
[4] The quantitative determination of the change in volume will be the object of a later investigation.
[5] Elliott and Lippmann, *J. Applied Physics* **16**, 50 (1945).
[6] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1934).
[7] Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935).
[8] Meyer, "Die hochpolymeren Verbindungen", Akad. Verlags-Ges., Leipzig, **1940**, p. 139.
[9] Compare Equations 38 and 39 of Elliott and Lippmann (see Reference no. 5).
[10] Holt and McPherson, *Bur. Standards J. Research* **17**, 657 (1936).
[11] Scott, *Bur. Standards J. Research* **14**, 99 (1935).
[12] Van der Wyk and Kuhn (*Helv. Chim. Acta* **29**, 1615 (1946)) do not take any account of the considerable changes in internal energy for low elongations. These changes in energy were, nevertheless, reported as far back as 1935.
[13] Roth and Wood, *J. Applied Physics* **15**, 749 (1944).
[14] Woods, *Nature* **157**, 229 (1946).
[15] Gee, *Trans. Faraday Soc.* **42**, 585 (1946).

MECHANISM AND THEORY OF VULCANIZATION *

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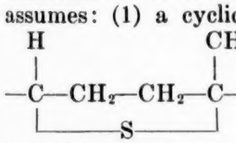
Rubber was used commercially before the discovery of vulcanization because of its elastic properties. Guth and Mark[1], Kuhn[2], Wall[3] and others have shown that this elasticity does not depend on vulcanization nor is it peculiar to Hevea rubber, but is characteristic of any material which is composed of long-chain molecules with freely rotating valence bonds and in which the intermolecular forces are comparatively weak. Thus, it was not the search for elasticity but rather the search for a means to overcome the undesirable thermoplastic properties of rubber that led to the discovery of vulcanization.

As a result of extensive experimentation (not by accident as popularly believed), Goodyear[4] found in 1839 that rubber does not become hard and stiff (frozen) at low temperatures or soft and sticky at high temperatures if 100 parts of rubber, mixed with 20 parts of sulfur and 28 parts of white lead, are heated at 270° F. He believed that the rubber combines with both the sulfur and with the lead compounds to form a triple compound in the process and that the lead can be added in the form of its salts or oxides, although some are more effective than others. Following Goodyear, no other hypothesis was advanced for the vulcanization reaction until the work of Henriques[5] and Weber[6]. Since then many theories of vulcanization, both physical and chemical, have been advanced. These theories have been ably reviewed by Kindscher[7], Williams[8], Fisher[9], LeBras and Compagnon[10], and van Amerongen and Houwink[11]. Of the theories proposed, the one most prevalently held today assumes: (1) a cyclic structure for hard rubber vulcanization of the type



; and (2) some form of sulfur or oxygen bridge, linking the rubber molecules by primary-valence bonds in soft rubber vulcanization—for example, R—S—R—S—R.

To explain the effects of inorganic and organic accelerators on the vulcanization reaction, elaborate theories have been proposed, most of which assume that these materials act as catalysts in a reaction mechanism that effects the linking of rubber molecules by sulfur bridges or other types of primary-valence forces. As pointed out by Williams[8], the theories of vulcanization that have been proposed do not explain the facts adequately and are subject to many objections. In view of the inadequacy of existing theories, studies of the mechanism of the vulcanization reaction were undertaken in 1939 in The B. F. Goodrich Company laboratories.

In surveying the literature on vulcanization, the present authors noted that there were at least two, and generally three, requirements for vulcanization of

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any natural or synthetic rubber. Preliminary experiments confirmed this conclusion. These requirements which must be explained in any adequate theory of vulcanization are as follows.

1. Ethylenic double bonds (—C=C—) must be present in the polymer molecule. Completely saturated polymers, such as polyethylene, polyisobutylene, polystyrene, and hydrogenated natural or synthetic rubber, cannot be vulcanized with the usual vulcanizing agents, whereas natural rubber, polyisoprene, polybutadiene, and copolymers of isoprene or butadiene, which are unsaturated polymers to varying degrees, can be vulcanized.

2. An oxidizing agent is required which adds in some manner to the double bonds or alpha-methylene carbon atoms in the polymer molecule to produce strong polar groups on the molecule. In addition to sulfur, some of the oxidizing agents that are suitable for vulcanization are certain of the thiuram disulfides, accelerator-sulfur complexes, organic nitro compounds, and quinones. Judging from published data, peroxides apparently cause a polymerization type of reaction rather than vulcanization in the sense used in this paper.

3. A divalent metallic compound is required to develop the best properties of the vulcanizate. In some instances vulcanizates can be prepared with only an unsaturated polymer and an oxidizing agent; nevertheless, the properties of the vulcanizate are greatly enhanced when a soluble divalent metallic compound is present. With many oxidizing agents the use of such compounds is imperative.

It is evident from the published data that vulcanization is a typical chemical reaction and that it obeys all the laws for such reactions. It appeared from a study of the literature and the data reported later in this paper, that the principal factors which affect the vulcanization reaction are: (1) the temperature of the reaction; (2) the pH of the system; (3) the solubility of the oxidizing agent and the divalent metallic compounds; (4) the effective concentration of these substances if they are below the saturation level; and (5) the chemical nature of the vulcanizing agent.

Further, it became apparent that cross-linking of rubber molecules by primary-valence bonds is not the explanation of ordinary vulcanization. Consequently, the conclusions of Goodyear[4], Midgley, Henne, and Shepard[12], Williams[13], and of the study reported here were developed into a theory of vulcanization whereby the sulfur, accelerator, and divalent metallic ion (or the vulcanizing ingredients in other types of vulcanization) react with, and become a part of, the rubber molecule. Through the increase in the intermolecular forces resulting from dipole interaction and ionic valences of the polar groups so introduced into the rubber molecules, the effects of vulcanization on the physical properties are explained.

PROCEDURE

Most of the studies were made on first-grade pale crepe, since this material was more uniform and had less objectionable impurities than any other material available at the time this work was done. Particular care had to be taken to avoid contamination of the compounds with dust from the mill room. Traces of zinc compounds were found to have a pronounced effect on the properties of the vulcanizate. The rubber vulcanizates were prepared by mixing on a 6 × 12-inch laboratory rubber mill and cured into 6 × 8 × 0.030 to 0.100-inch tensile sheets in the usual manner.

The vulcanization reaction was followed by means of the stress strain properties of the vulcanizate and the x-ray diffraction patterns of the curing ingredients in the rubber compound at various stages of vulcanization. The x-ray diffraction patterns were obtained by a technique similar to that used by Clark, Le Tourneau, and Ball[14].

The acid-base characteristics were determined in a few of the compounds by passing the vulcanizate twice through tight rolls of a cold laboratory mill, extracting the crumb so obtained with freshly distilled cyclohexanone for 16 hours at room temperature, and measuring the pH of the extract with a glass electrode and a Leeds & Northrup pH electrometer. These pH measurements were in agreement with those obtained by dissolving the uncured compound in freshly distilled cyclohexanone and heating the solution 60 minutes at 150° C to effect cure. Most of the measurements were made by the latter technique, since the pH could be measured after various times of heating.

RESULTS

Vulcanizing agent constant with zinc variable.—As seen in Table I, the stress at 700 per cent elongation increased thirteenfold, and the ultimate elongation decreased by one-third as the concentration of zinc ions (the term "ions" used throughout this paper refers to both those that are free and those combined in the form of salts) increased from zero to an amount molecularly equivalent to the 5 parts of Tuads (tetramethylthiuram disulfide) in the compounds. When the vulcanizates indicated in Table I were examined by x-rays, diffraction

TABLE I

EFFECT OF ZINC ION IN RUBBER-TUADS RECIPE

Recipe	Zinc/tuads mole ratio	Tensile strength (lb./sq. in.)	Elongation (%)	700% modulus (lb./sq. in.)
Control (basic recipe*)	0	2200	1060	200
Zn stearate $\approx$ 0.25 Tuads	0.05	2500	980	350
Zn stearate $\approx$ 0.50 Tuads	0.1	2300	960	300
Zn stearate $\approx$ 1.00 Tuads	0.2	2200	910	500
Zn stearate + ZnO $\approx$ 2.00 Tuads	0.4	2400	850	800
Zn stearate + ZnO $\approx$ 5.00 Tuads	1.0	2800	710	2600
Zn stearate + ZnO $\approx$ 8.00 Tuads	1.6	2900	710	2700

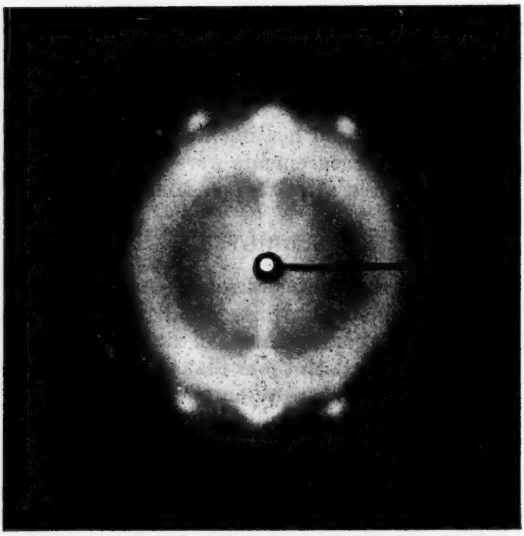
* Pale crepe 100 parts, Tuads 5 parts. Other recipies had the ingredients indicated added to the basic recipe. Equivalents indicated were on a molecular basis. All compounds were cured 30 minutes at 280° F, which was near or at the optimum cure in all instances.

patterns of crystalline Zimate (zinc dimethyldithiocarbamate) were obtained in all instances except with the control compound and with the one containing the smallest quantity of zinc stearate. In addition, patterns for zinc oxide were observed in the two vulcanizates containing the highest concentration of zinc ions.

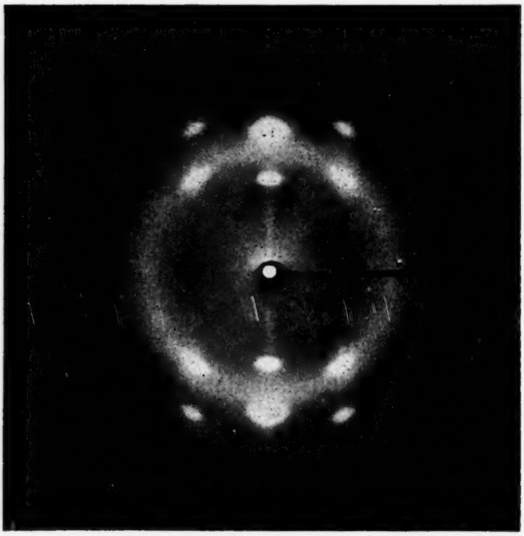
In similar studies on compounds containing pale crepe 100 parts, sulfur 10 parts, and varying quantities of zinc oxide, the stress at 700 per cent elongation doubled and the ultimate elongation decreased by one-tenth as the concentration of zinc oxide increased from 0 to 0.75 per cent.

It was noted that, in the x-ray diffraction patterns of the stretched rubber-sulfur stock (without zinc), the A_1 and A_2 spots were approximately circular in shape (Figure 1A), whereas in those of the stretched rubber–Tuads compound

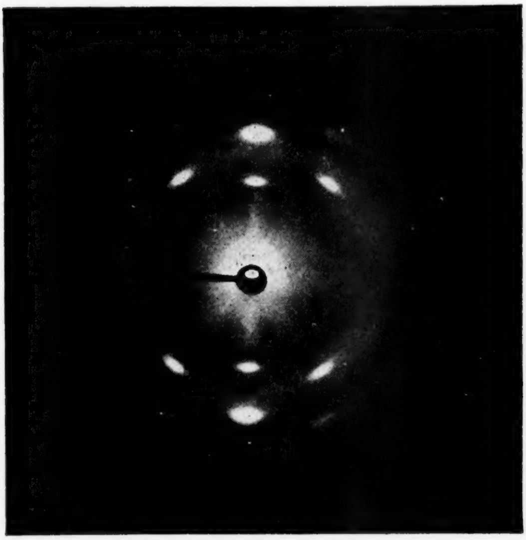
(without zinc) these spots were elliptical (Figure 1*B*), with the minor axis perpendicular to the direction of stretching. The presence of zinc ions increased the eccentricity of the spots for both types of vulcanizate (Figure 1*C* and *D*) in a manner similar to but smaller in magnitude than that due to carbon black.



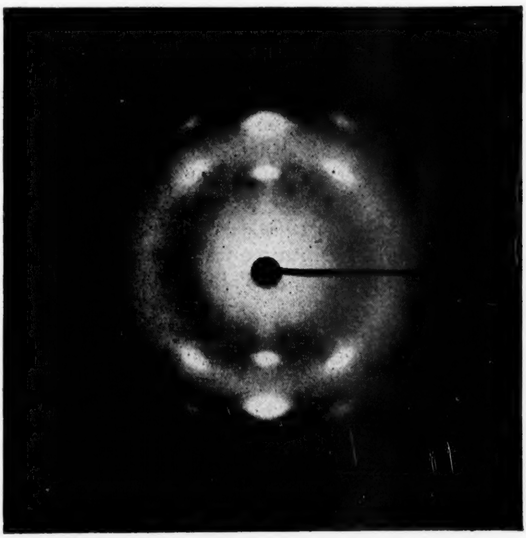
A. Pale crepe 100, sulfur 10, cured 120 minutes at 300° F.



B. Pale crepe 100, Tuads 5, cured 30 minutes at 280° F.



C. Pale crepe 100, sulfur 10, zinc 0.75, cured 120 minutes at 300° F.



D. Pale crepe 100, Tuads 5, zinc stearate 2.65, cured 30 minutes at 280° F.

FIG. 1.—*x*-Ray diffraction patterns of compounds at 600% elongation.

Zinc constant with sulfur variable.—As seen in Table II, increasing the concentration of sulfur from 0.5 to 2 parts per 100 parts of pale crepe had little or no effect on tensile properties when the zinc ion in the form of Zimate was kept constant. It was interesting to observe that the stress-strain properties im-

mediately after curing were very poor when Zimate was the only source of zinc ion. However, after the vulcanizates had aged for four months at room temperature, tensiles of 1200 pounds per square inch or more were obtained. The tensile of vulcanizates cured 5 minutes at 280° F increased from 400 or less to 1500 pounds per square inch for the compound containing 0.5 part sulfur and 2200 pounds or more for the others.

Table II

Effect of Sulfur in Rubber-Zimate Compounds

	Tensile strength (lb./sq. in.)		Elongation (%)	
Sulfur*	Original	Aged 4 months	Original	Aged 4 months
0.5	400	1200	1250	1120
1.0	600	1300	1240	1230
1.5	600	1300	1220	1060
2.0	400	1600	1210	1130

* Recipe, pale crepe 100 parts, Zimate 1 part, plus sulfur indicated. Data given for vulcanizates cured 30 minutes at 280° F.

The x-ray diffraction patterns indicated that Zimate had disappeared completely in all compounds cured 30 minutes at 280° F, and by amounts proportional to the sulfur present in those cured 5 minutes at 180° F. Figure 2 shows the disappearance of Zimate during cure. The circular arcs in Figure 2*A* are the diffraction patterns of Zimate in an uncured stretched rubber specimen containing 2.5 per cent of Zimate and 1 per cent of sulfur. These arcs have disappeared in Figure 2*B*, which is the diffraction pattern of the same compound cured 30 minutes at 280° F and then stretched. At the end of four months Zimate could not be detected in any vulcanizate except the one containing 0.5 part sulfur cured 5 minutes at 280° F. In another compound containing 1.3 per cent Zimate and 0.2 per cent sulfur the pattern for Zimate completely disappeared when the compound was heated 30 minutes at 280° F. This was the smallest amount of sulfur that made the patterns for Zimate disappear; this indicated a probable combining ratio of 2 atoms of sulfur to 1 molecule of Zimate.

Comparison of divalent metallic oxides.—A comparison of the relative effects of zinc, lead, calcium, and magnesium oxides was made in both rubber-Tuads and rubber-Tuads-sulfur compounds. Table III presents the data for the

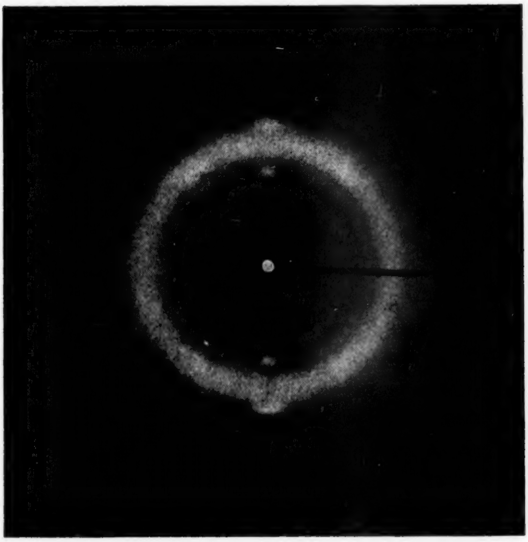
Table III

Influence of Oxides of Calcium, Magnesium, Zinc, and Lead in Rubber-Tuads Compounds

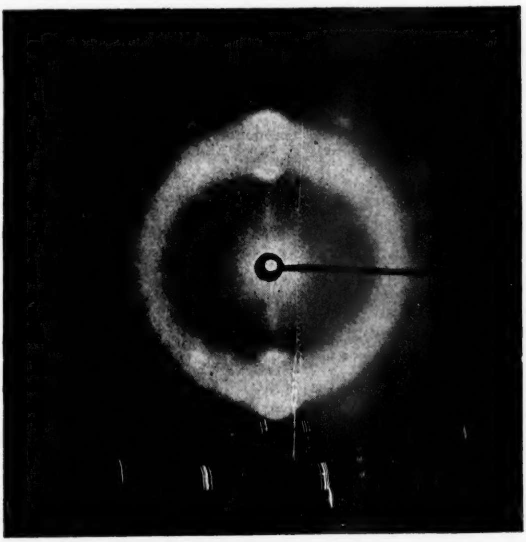
Recipe	Tensile strength (lb./sq. in.)	Elongation (%)	700% modulus (lb./sq. in.)
Control (basic recipe*)	1200	800	600
Stearic acid 5	800	860	400
Stearic acid 2, $Ca(OH)_2$ 3.5	2400	830	1200
Stearic acid 2, MgO 2	2300	900	700
Stearic acid 2, ZnO 3.5	2700	730	2100
Stearic acid 2, PbO 10	—	—	—

* Pale crepe 100 parts, Tuads 5 parts. Other recipes had the ingredients indicated added to the basic recipe in parts by weight. The quantities of metallic oxides were equivalent on a molecular basis. All compounds were cured 25 minutes at 280° F.

rubber-Tuads compounds. Except for lead oxide, all of these oxides increased the modulus and tensile strength. The calcium and magnesium oxides in-



A. Uncured.



B. Cured 30 minutes at 280° F.

FIG. 2.—x-Ray diffraction patterns of compounds containing pale crepe 100, Zimate 2.5, sulfur 1 and stretched to 600% elongation.

creased the rate of cure markedly, and the overcures reverted badly. The lead oxide was completely converted to Ledate (lead dimethyldithiocarbamate) and lead stearate. Figure 3 is an x-ray diffraction patern of a stretched rubber-

Tuads-lead oxide compound heated 45 minutes at 300° F, showing the formation of oriented Ledate.

Similar results were obtained for the rubber-Tuads-sulfur stocks, except that the compound containing lead oxide cured and had higher modulus and lower elongation than the control. The recipes for these compounds were: pale crepe 100 parts, Tuads 3 parts, sulfur 0.75 part, plus the oxide under test

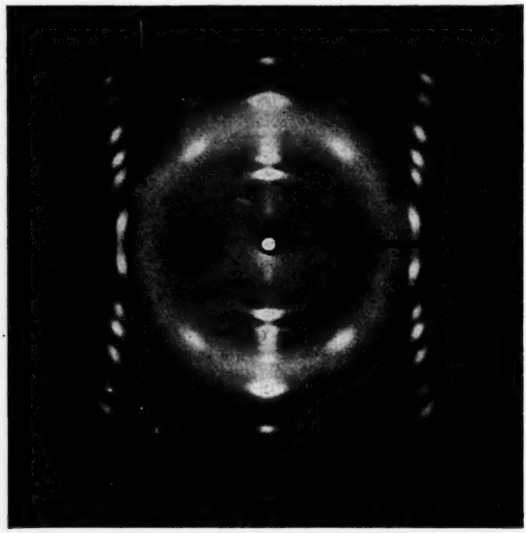


FIG. 3—x-Ray diffraction pattern of compound containing pale crepe 100, Tuads 5, lead oxide 2.3, cured 45 minutes at 300° F and stretched to 600% elongation.

and stearic acid in the same quantities as given for the corresponding compounds in Table III. In both series of compounds the rate of curing was in the order: lead (slowest), Tuads or Tuads-sulfur control, zinc, magnesium, and calcium (fastest). Lead and zinc stearates were observed in the patterns, whereas calcium and magnesium stearates were not. When caproic acid was substituted for the stearic acid, no pattern of lead or zinc caproate was observed, and the rate of curing was markedly increased.

Effect of various anions.—The results obtained in studying the effect on the physical properties of rubber–Tuads compounds, when the metal is added in the form of different salts, are given in Table IV. Zinc added in the form of any salt increased both modulus and tensile. In all instances Zimate was formed, and the added zinc compound disappeared completely except for traces of zinc sulfide. Both the sulfide and sulfate retarded cure but enhanced the physical properties. In the vulcanizates which were cured 5 minutes at 280° F and contained either zinc oxide or zinc stearate, the x-ray diffraction patterns gave evidence that a new compound was formed, which has not yet been identified. A similar pattern also was obtained with the precipitate formed after Zimate and cyclohexylamine were heated in xylene for 5 minutes at 110° C. As heating continued, Zimate was regenerated in the solution when insufficient cyclohexylamine was present; a small particle-size crystallite was formed with larger amounts of cyclohexylamine.

A pattern for stearic acid was obtained in the compound to which zinc stearate had been added. In another experiment in which the zinc was added in the form of Zimate instead of zinc stearate, a similar increase of the stress-strain properties was noted, except that double the quantity of zinc ion on a molecular basis was required to obtain an equivalent effect.

TABLE IV

EFFECT OF ZINC AND LEAD ADDED IN FORM OF DIFFERENT SALTS AND IN CONJUNCTION WITH ACID ON PROPERTIES OF RUBBER-TUADS COMPOUNDS

Recipe	Cured at 280° F (min.)	Tensile strength (lb./sq. in.)	Elongation (%)	700% modulus (lb./sq. in.)
Control *A* (basic recipe*)	30	1200	940	300
ZnO	30	2600	870	800
ZnS (alpha)	30‡	2200	930	400
$ZnSO_4 \cdot 7H_2O$	30‡	1700	870	500
Zn stearate	30	2500	820	1000
PbO	45	900	820	500
PbS	45	700	1100	200
$PbSO_4$	45	800	1050	200
Pb stearate	30	1300	1050	300
Trichloroacetic acid	30	1200	960	300
Trichloroacetic acid + ZnO	30	2500	860	900
Trichloroacetic acid + PbO	45	700	1000	200
Benzoic acid	30	1400	1100	300
Benzoic acid + ZnO	30	2300	820	1000
Benzoic acid + PbO	45	600	820	250
Control B†	30	600	1050	150

* Pale crepe 100 parts, Tuads 5 parts. Other recipes had ingredients as indicated in an amount equivalent to 2.5 parts Tuads on a molecular basis, added to the basic recipe.
† Control *B* had 2.5 parts instead of 5 parts of Tuads in the recipe.
‡ Below optimum cure.

All the compounds with lead had higher tensiles and moduli than control *B* containing 2.5 parts of Tuads, but not so high as those of control *A* with 5 parts of Tuads, except for the modulus of the compound containing lead oxide. The rate of cure was less in all instances also. The patterns for all the lead compounds added had disappeared, and Ledate patterns were observed in every instance. Trichloroacetic or benzoic acid in combination with zinc or lead oxide caused effects similar to those with the corresponding stearates.

The particle size and the intensity of the *x*-ray diffraction patterns of the Zimate or Ledate formed gave a qualitative indication of the solubility rate and, hence, indirectly of the solubility of the zinc or lead compound added. The finest particle size, related to the greatest solubility, was observed for the stearates, followed by the oxides (presumably made soluble by the fatty acids in the rubber), sulfates, and sulfides.

Addition and removal of divalent metallic ions from rubber vulcanizates.—The *x*-ray diffraction patterns of the rubber vulcanizates described thus far and the results given in Tables I to IV indicated that the accelerator and the divalent metallic ion were combining with the rubber molecule. It was, therefore, decided to test this conclusion by observing the effect on the properties of the vulcanizate when zinc or lead ions were introduced into or removed from the vulcanizate after curing. The metallic ions were introduced into the vulcanizate by treating the surface with a metallic stearate, as follows. A rubber-sulfur or rubber-Tuads vulcanizate at optimum cure was coated on the surface

with the stearate and then heated for 30 minutes at a temperature 50° F below the curing temperature. The control was similarly heated, but not treated with the stearate. The stearates were molten at these temperatures and partially dissolved in the thin sheets (0.030 inch approximately). The metallic ions were removed from the molecular structure by soaking the vulcanizate in a dilute aqueous solution of hydrochloric acid or trichloroacetic acid for several days at room temperature, while the control was similarly treated with distilled water. After soaking, the specimens were allowed to dry thoroughly before testing. Hydrochloric acid was not very effective for this purpose, evidently because of its complete ionization in water, which prevented penetration of the acid into the rubber vulcanizate. This experiment should be repeated with the hydrochloric acid dissolved in anhydrous alcohol.

Table V presents the results obtained by surface treatment of vulcanizates with zinc and lead stearates, and by soaking vulcanizates in trichloroacetic acid. When a vulcanizate containing no divalent metal was surface-treated with zinc, increased moduli were obtained, whereas when a vulcanizate containing zinc was soaked in trichloroacetic acid, decreased moduli resulted. Similar effects were noted in the case of lead. However, the rubber-sulfur vulcanizate surface-treated with lead stearate did not respond like the others, apparently because of the formation, with the unreacted sulfur, of insoluble lead sulfide near the surface, since no attempt was made to extract the free sulfur remaining after cure before surface treating with lead stearate. Larger effects than those given in Table V for rubber-Tuads vulcanizates surface-treated with lead stearate, were obtained in other experiments.

Traces of Zimate and Ledate were noted in the x-ray diffraction patterns of the rubber-Tuads vulcanizate that was surface-treated with the corresponding stearates. It was interesting to observe that lead stearate added to a rubber-Tuads compound before vulcanization retarded cure and decreased the modulus, whereas lead stearate added after vulcanization increased the modulus. Trichloroacetic acid treatment of the control, containing Tuads and zinc stearate, reduced the intensity of the sharp crystalline x-ray diffraction pattern of the

TABLE V

INTRODUCTION BY SURFACE TREATMENT AND REMOVAL BY ACID TREATMENT OF ZINC AND LEAD IN RUBBER-TUADS AND RUBBER-SULFUR COMPOUNDS

Recipe* and treatment	Tensile strength (lb./sq. in.)	Elongation (%)	700% modulus (lb./sq. in.)
S 10, control	2400	860	900
Same, Zn stearate on surface	2400	830	1000
Same, Pb stearate on surface	1700	800	900
Tuads 5, control	1500	1130	200
Same, Zn stearate on surface	1800	820	600
Same, Pb stearate on surface	1500	950	350
S 10; Zn stearate 4.5, control	2000	750	1400
Same, soaked in aqueous TCA†	3000	310	—
Tuads 5, Zn stearate 2.65, control	2900	900	600
Same, soaked in aqueous TCA†	2200	900	350
S 10, Pb stearate 5.5, control	2000	980	400
Same, soaked in aqueous TCA†	1750	960	350
Tuads 6; Pb stearate 3.2, control	1700	1090	200
Same, soaked in aqueous TCA†	1300	1100	150

* Ingredients indicated are in parts by weight per 100 parts of pale crepe; optimum cure was selected in each instance.

† Approximately 0.2 N trichloroacetic acid.

rubber so that it was similar to one for a rubber-sulfur vulcanizate. The Zimate pattern was barely visible.

Influence of pH.—A qualitative correlation was noted between the rate of vulcanization and the pH of the heated cyclohexanone cement or the extract of the vulcanizate given in Table VI. The compound containing cyclohexylamine cured in the least time but reverted quickly. With other compounds not

TABLE VI

pH OF VULCANIZED CEMENTS AND VULCANIZATE EXTRACTS

Recipe*	pH of 5% cement in cyclohexanone: Control unheated	Heated at 305° F (60 min.)
S 10	4.9	3.6†
S 6, PbO 10, stearic acid 1	7.2	3.6
S 6, DPG 1	5.6	3.9
S 6, DPG 1, ZnO 2	6.2	4.6
S 1, ZnO 2, S.A. 1, Captax 1	6.3	5.3
Same plus cyclohexylamine 1	6.9	7.3
S 1, ZnO 2, S.A. 1, Captax 1, Tuads 0.2	6.0	6.1‡
S 1, PbO 6, S.A. 1, Captax 1, Tuads 0.2	6.7	5.9§
Tuads 5	7.0	7.1
Tuads 5, ZnO 2	7.0	7.1

* Basic recipe, pale crepe 100 parts plus ingredients indicated.
† pH of cyclohexanone extract of vulcanizate cured 60 minutes at 320° F, 3.8; pH of cyclohexanone extract of similar vulcanizate but containing 4.5 parts of zinc stearate in addition, 4.4.
‡ pH cyclohexanone extract of vulcanizate cured 30 minutes at 280° F, 6.2; pH cyclohexanone extract of vulcanizate cured 60 minutes at 300° F, 6.4.
§ pH cyclohexanone extract of vulcanizate cured 30 minutes at 280° F, 5.8; pH cyclohexanone extract of vulcanizate cured 60 minutes at 300° F, 5.8.

reported here, there were indications that, above a pH of 8, reversion occurred so soon that a satisfactory vulcanizate could not be obtained. On the contrary, the compound containing only sulfur cured the slowest, and there were indications that acids which reduced the pH below 3 retarded vulcanization so markedly that cure could not be attained. It is to be emphasized that a given pH in cyclohexanone solution is not necessarily equivalent to the same pH in an aqueous solution.

Hydrogen sulfide was liberated from the cement, when treated, in every instance in which free sulfur was present, and no hydrogen sulfide could be detected in the two cases given in Table VI where Tuads but no sulfur was present. The total amount of hydrogen sulfide liberated correlated qualitatively with the amount of free sulfur added; however, the rate at which it was liberated increased with pH. In rubber cements containing litharge and sulfur it was noted that lead sulfide was formed, but in those containing zinc oxide no zinc sulfide was detected.

DISCUSSION

Evidence against cross-linking through primary valences.—The experimental results indicate that divalent metallic compounds have a definite influence on the crystalline structure and physical properties of rubber in a manner independent of any effect they may have on the rate of cure. The effect of these substances in Tuads vulcanizates indicates further that vulcanization is not solely a cross-linking of rubber molecules with sulfur or other primary valence bonds, but rather that both the Tuads and metallic ion become a part of the structure of the rubber molecules. In fact, the experiments of Williams[15]

indicate that, even in a rubber-sulfur vulcanizate, cross-linking of rubber molecules by primary-valence bonds does not occur. He found that smoked sheet containing 6 per cent of sulfur, vulcanized for 75 minutes at 150° C, swells in benzene but does not lose its shape or dissolve in 15 days. Adding to the benzene such compounds as piperidine, mercaptobenzothiazole, the piperidine salt of mercaptobenzothiazole, butyraldehydebutylamine reaction products, or other accelerators causes either a marked visible effect or a homogeneous solution in the same period of time. Soluble zinc salts added to the benzene retarded the action of these materials. If a three-dimensional network through primary-valence bonds formed during vulcanization, it is difficult to explain these results. However, even if it is assumed that a few rubber molecules are cross-linked by primary-valence bonds through sulfur or oxygen bridges during vulcanization, it is evident from the work of Midgley, Henne, and Shepard[12], in which rubber was treated with Grignard reagents, that cross-linking of rubber molecules by primary valence bonds is not essential to obtain vulcanization.

Evidence against cross-linking by primary-valence bonds, in addition to that presented by Williams[16], is as follows.

1. In polymers with very few double bonds—for example, GR-I—it is improbable that a sufficient number of double bonds or alpha-methylene carbon atoms in different molecules are adjacent and properly oriented so they can be bridged by sulfur to form a satisfactory vulcanizate.

2. The sulfur bridge would have to be formed in two or more steps, since trimolecular reactions have not been demonstrated. It should be possible to prevent the cross-linking, therefore, by the addition of reactive compounds, particularly if a free-radical chain mechanism were involved. Although many compounds have been found which accelerate vulcanization, no compound, except those lowering the pH, has been found which retards the sulfur type of vulcanization reaction. In Tuads vulcanization even acids do not decrease the rate.

3. The fibrous structure which develops on stretching would be expected to decrease as the number of primary cross-linkages increased during vulcanization. Well cured compounds, particularly those containing channel black, still develop fibrous structures as pronounced as those in crude rubber. The forces between the fibers or molecules are very small compared to those between atoms in the molecules themselves. This can be easily demonstrated by inserting a pin in a piece of stretched rubber and moving it both parallel and perpendicular to the direction of stretch. The force required to move the pin parallel to the direction of stretch is negligible compared with that required to move it perpendicular to this direction.

4. If organic accelerators and divalent metallic ions do not become a part of the rubber molecule along with the sulfur but only activate the sulfur to cross-link the rubber molecules, these compounds should not improve the properties of a three-dimensional network already formed by vulcanization. This is contrary to the results in Table V and those reported by Williams[17].

5. In cases where cross-linking by primary-valence bonds is fairly certain, the polymers lose their rubberlike elasticity and become resinous. For example, resinification of polybutadiene or butadiene copolymers, prepared by emulsion polymerization, occurs if the polymerization catalyst is not completely destroyed after polymerization. Certain types of photovulcanization and peroxide vulcanization are probably also polymerization rather than vulcaniza-

tion reactions. Divalent metallic oxides do not assist these reactions and frequently retard them.

6. The stress-strain temperature effects, particularly the large hysteresis of the first cycle of flexing, noted by Roth and Wood[18], Meyer and Ferri[19], and Holt[20], indicate that it is relatively easy to rearrange the intermolecular forces, and that the forces involved must be relatively small and of several strengths. The changes observed were reversible to a first approximation. It is difficult to understand how primary-valence bonds could be so easily broken and rearranged without showing evidence of more drastic and permanent changes in the stress-strain properties, such as those produced by oxygen on aging. Particularly, it does not seem reasonable to expect an increase in stress with time following a reduction of elongation if primary-valence bonds are responsible.

7. It is not reasonable to assume that primary bonds between rubber molecules are formed in the early stages of vulcanization and then broken during overcure and reversion.

8. As pointed out by van Dalfsen[21], the properties of films from vulcanized latex must result from secondary valence forces and not from those of primary-valence bonds.

Reaction of rubber with compounds other than sulfur.—In the presence of a number of reactive compounds, either naturally occurring in or added to the rubber, it is not valid to assume that the rubber molecule reacts exclusively with the sulfur. As mentioned previously, the data indicate the converse—namely, that the rubber does react with compounds other than sulfur. These conclusions are further substantiated in vulcanization with aromatic nitro and azo compounds, during which Blake[22] and Fisher[9] have shown that nitrogen is combined in some form with the rubber. With sulfur compounds, such as Tuads, evidence of this type has not been reported. However, Wistinghausen[23] found that both diphenylguanidine and mercaptobenzothiazole disappeared during vulcanization.

The results reported herein, and those obtained by Clark, Le Tourneau, and Ball[14], indicate conclusively that carbon disulfide accelerators react during the early stages of vulcanization with metallic compounds to form metallic salts of the accelerator. The question still remains how these salts of accelerators react with the sulfur and form a compound with the rubber molecule. There appears to be little doubt that they do, however, since it was noted that (1) when the various salts, Zimate, Zenite, Ledate, etc., were added to rubber as such or were formed in the rubber by interaction between the acid form of the accelerator and a metallic compound, their x-ray diffraction patterns decrease in intensity after the early stages of cure and disappear completely in the latter stages if excess quantities are not added; (2) neither the metallic ion nor accelerator anion could be detected in other crystalline compounds; and (3) the diffraction pattern of the rubber crystallites became altered in shape. Even lead oxide, when heated with acetone-extracted pale crepe, reacts with the rubber or unextractable materials in it to form a new compound.

An interesting observation in connection with the reaction of compounds other than sulfur has been made during the vulcanization of balata, using the same recipes and conditions found to be optimum with Hevea. It was noted that vulcanization of balata with sulfur and diphenylguanidine (DPG) or di-*o*-tolylguanidine (DOTG) had a more striking effect on the retention of rubberlike elasticity at room temperature than vulcanization with sulfur,

either in the presence or absence of carbon disulfide accelerators and(or) zinc oxide. Heating balata with DPG or DOTG in the absence of sulfur under equivalent conditions of time and temperature failed to produce a soft structure after cooling to room temperature. To achieve an equivalent effect with other vulcanizing agents, a higher degree of cure was required. These observations indicated that more than a combination of balata and sulfur was involved, and that the DPG, sulfur, and balata had combined in some manner to form an integrated structure.

Solubility and rate of cure.—There is a direct correlation in rubber-Tuads compounds between rate of cure and solbuility of the metallic salts, as judged by the particle size of the Ledate or Zimate formed; for example, zinc stearate produced the finest particle-size Zimate, best physical properties, and fastest rate of curing, whereas zinc sulfide produced the largest Zimate particles, poorest properties, and slowest rate of curing. None of the zinc or lead compounds studied is completely insoluble and inert in rubber. Consequently by altering conditions it is possible to shift the equilibrium; for example, Ledate in the presence of excess sulfur forms lead sulfide with no Ledate remaining, whereas lead sulfide in the presence of excess Tuads forms Ledate with no lead sulfide remaining. Jones and Depew[24] were led to similar conclusions regarding the effect of solubility of lead and zinc compounds on rate of cure. These workers found that even the order of adding ingredients affects the rate of curing when an ingredient is formed in the rubber compound which is only slightly soluble, and that the equilibrium can be shifted by increasing the concentration of the more soluble components. In compounds accelerated with mercaptobenzothiazole, these workers showed effectively that the properties of the vulcanizate depend on the amount of soluble zinc available for reaction, which is a function of the amount both of fat acid or zinc soap and of amines such as diphenylguanidine or butyraldehydeaniline in the rubber compound. Cotton and Westhead[25] showed in an extensive study of the influence of various metallic oxides on vulcanization that zinc and lead oxides are not unique in their effect on vulcanization and that some oxides are more effective than others. It is probable that the differences in the effects of the various oxides result from differences in the solubilities of the various metallic salts formed during the vulcanization reaction.

The most pronounced difference between zinc and lead compounds in rubber containing sulfur is in the formation of the sulfide. Lead compounds form lead sulfide with ease, which is readily precipitated because of its low solubility. Zinc compounds, on the other hand, apparently do not form zinc sulfide, since no patterns of alpha or beta zinc sulfide have been observed despite the relatively low solubility of these materials when added to rubber. The results obtained with rubber in xylene indicate that this is due to the strength of hydrogen sulfide as an acid, and lead and zinc stearates as bases. These observations are not in accord with the conclusions of Armstrong, Little, and Doak[26], who assumed that the hyrogen sulfide liberated during the digestion of a vulcanizate with glacial acetic and concentrated hydrochloric acids is derived from zinc sulfide. They suggested that the zinc sulfide is derived from a zinc mercaptide of the rubber, momentarily formed as an intermediate during the vulcanization process. Therefore, they assume that the amount of zinc sulfide formed is a measure of the number of thioether or disulfide linkages between the rubber molecules. From our observations we cannot concur in the opinion that significant quantities of zinc sulfide are formed or that rubber molecules

are linked by primary-valence bonds. As will be seen, we propose a zinc mercaptide of the rubber in our theory of vulcanization but not under the conditions stated by Armstrong, Little, and Doak[26].

A correlation between solubility and rate of curing is noted also with butadiene copolymers. Zimate is most soluble in the acrylonitrile copolymers, next in vinylidene chloride copolymers, and least soluble in methyl methacrylate copolymers. The rate of curing corresponds to these solubilities. In each polymer cyclohexylamine increased the solubility of Zimate and the rate of cure. The lack of amino compounds in synthetic rubbers for solubilizing zinc salts is probably responsible for the commercial use of multiple accelerators, generally a carbon disulfide accelerator, a basic amine, and zinc oxide.

The solubilities observed in these studies are those at room temperature. To make a quantitative analysis of the physical-chemical system during vulcanization, it is necessary to measure these solubilities at vulcanizing temperatures.

Other physical-chemical factors.—When solubility is not the principal limiting factor, the relative strengths and concentrations of the various acids and bases in the system have a direct bearing on the rate of curing and the physical properties of the final vulcanizate. To ensure a satisfactory cure and good physical properties, it is necessary that a sufficient quantity of divalent metallic ions be available for the rubber. The quantity of available ions is governed not only by the total number present but also by the concentration and relative strengths (pK values) of the other competing acids in the system. In low zinc stocks—for example, where the zinc has been introduced only as a salt of an organic accelerator—it has been found that poor physical properties result when stearic or other acids, competing with the rubber, combine with the zinc ions to form zinc salts. x-Ray diffraction patterns of such vulcanizates have confirmed the formation of zinc stearate. By adding sufficient zinc to satisfy all the acids present, the best properties are obtained.

Besides the strength of the acid, the pH of the system is the other factor governing the proportion of the acid which combines with zinc if all components are soluble. It has long been known that acids retard and bases accelerate sulfur vulcanization. However, the first quantitative correlation between pH and rate of curing was reported by Newton[27] and Newton and Wilson[28], who showed that the rate of curing of crude rubbers increased with the pH of their aqueous extracts, with their buffer capacity, and with the pH of phosphate buffers added to the rubber. Their results and those reported here indicate that in a rubber-sulfur system pH and buffer capacity are next in importance to temperature in governing rate of curing.

When the work was interrupted, the studies on the effect of monovalent metallic compounds had not been started. Work reported in the literature showed that some of these compounds have a profound effect on the rate of curing and the physical properties of the vulcanizate. Although definite conclusions cannot be drawn at this time, it is believed that the monovalent metallic compounds affect vulcanization primarily through their influence on the pH of the system. No trivalent metallic compounds were studied, but such compounds, if soluble, should behave like divalent compounds.

THEORY OF VULCANIZATION

The observations made and conclusions reached in the course of these studies led to the formulation of a theory of vulcanization. It is believed that

crude rubber is a highly unsaturated fatty acid of high molecular weight. Other studies on the pH titration and viscosity of cements prepared from pale crepe milled for various times indicate that there is a —COOH group on at least one end of the rubber molecule, which makes the adjacent terminal double bond or alpha-methylene carbon atom more reactive, so that it probably reacts first in vulcanization. The thixotropic effect observed with crude rubber is probably due in large part to the association (hydrogen bonding) and disassociation of these terminal acid groups. The effect of polar substances, particularly basic ones, on the viscosity of uncured rubber solutions in hydrocarbon solvents results from their effect on the disassociation of these groups, which causes the rubber particles to become monomolecular.

The elasticity of rubber is related to the thermal motion of the molecules. However, the weak van der Waals forces between the molecules of crude rubber result in a very low modulus and permit plastic flow and rotation around single bonds, so that the molecules become aligned easily and crystallize.

Vulcanization in absence of divalent metallic ions.—When sulfur is mixed with rubber and the mixture heated, the sulfur reacts with the rubber molecule, probably at the alpha-methylene carbon atom, to form a thioketone. This assumption has support from infrared studies by Sears[29] and Sheppard and Sutherland[30], who reported a band at 10.4μ, which could be assigned to a C=S bond. It is noted that these workers also reported no apparent decrease in the intensity of the band assigned to the C=C bond. Further, it is observed that no one has been able to detect thiol (—SH) groups in vulcanized rubber. To explain these observations, resonance is postulated between two or more structures, such as

$$\begin{array}{ccc} | & | & \\ -\mathrm{C} & =\mathrm{C} & -\mathrm{C}- \\ & & \| \\ & & \mathrm{S} \end{array} \quad \text{and} \quad \begin{array}{ccc} | & | & \\ -\mathrm{C} & -\mathrm{C} & =\mathrm{C}-. \\ + & & | \\ & & \mathrm{S}- \end{array}$$

In any case, the polar groups introduced into the rubber molecules during vulcanization markedly increase the intermolecular forces by dipole interaction. When a sufficient number of polar groups are present, plastic flow becomes extremely small, the modulus is markedly increased, and free rotation of the molecules is retarded so that they do not align and crystallize unless an external stress is applied.

When vulcanization is effected with Tuads, an accelerator-sulfur mixture, organic nitro or azo compounds, etc., most, if not all, of the oxidizing agent adds to the rubber molecule forming strong acidic groups on it. Benzoyl and other organic peroxides probably act differently in that they effect true cross-linking of molecules by polymerization (rather than vulcanization) as indicated by Farmer and Michael[31]. On the other hand, the organic basic amino compounds that act as accelerators probably play a dual role, namely, (1) to increase the pH of the system, and (2) to combine with the rubber molecule and sulfur to form a strong polar group capable of hydrogen bonding. The combination of polar organic compounds with rubber causes the intermoledular forces to be increased probably by both dipole interaction and hydrogen bonding, so that very few groups need to combine with the rubber.

Vulcanization in presence of divalent metallic ions.—If a soluble divalent metallic compound is present in rubber-sulfur vulcanization, the mercaptide structure is enhanced, and this increases further the intermolecular forces through the ionic mercaptide valences—for example, (rubber)—S^- Pb^{++}—(soap anion). It is possible that some of the molecules become bridged through

the ionic valences of a metallic mercaptide salt, thus: (rubber)—S Pb^{++}—S—(rubber). Accordingly, fewer sulfur atoms need add to the rubber molecules to obtain the same modulus and other properties. Farmer[32] suggests a similar mercaptide bridge in rubber-sulfur-zinc oxide vulcanizates. However, like Armstrong, Little, and Doak[26], he assumes the mercaptide to be an intermediate in a cross-linking reaction.

When vulcanization is effected with polar organic compounds, the resulting acidic groups in the rubber molecule are stronger than the mercaptide groups in rubber-sulfur vulcanizates and form salts with the divalent metallic ion more readily. Accordingly, divalent metallic ions are much more effective with this type of vulcanization than with rubber-sulfur vulcanization, so that minimal quantities of vulcanizing agents are required, probably only the quantity needed to react with the terminal reactive groups of the rubber molecule. As with rubber-sulfur vulcanizates, two or more molecules may be bridged through the ionic valences of a divalent metallic salt, thus: (rubber)—(accelerator-S complex)$^{-}Zn^{++}$—(accelerator-S complex)—(rubber).

Factors influencing vulcanization.—The main factors which influence vulcanization either in the presence or absence of divalent metallic compounds are (1) temperature, (2) relative solubilities of the various components in the system, (3) nature and effective concentration of the vulcanizing ingredients, (4) relative strengths and concentrations of the acid groups in the system, and (5) pH of the system. The rate of curing is governed primarily by temperature, pH, and concentration of the vulcanizing ingredients, the rate increasing with an increase in the value of each of these variables. In the case of delayed-action accelerators, the active vulcanizing ingredient is released after vulcanizing temperatures are reached, so the effective concentration is very low during the initial vulcanization period. The properties of the vulcanizate are governed primarily by the nature of the vulcanizing agent, the degree of cure, and the concentration of divalent metallic ions in the rubber structure. The proportion of these ions in the rubber structure depends on the relative strengths and concentrations of the acid groups in the rubber compared to those of other acids present. The ions are partitioned among the acidic groups of the rubber and other acids present according to the laws of physical chemistry.

Thus, vulcanization is essentially a process whereby the intermolecular forces are increased by the introduction of polar groups into the rubber molecules at the double bonds or alpha-methylene carbon atoms. The individual molecules retain their identity with respect to length and approximate weight, although they may be joined to other molecules through the salt of a divalent metallic ion. The forces between the individual molecules give a rigidity to the molecular structure that retards plastic flow and crystallization, but are sufficiently weak to rearrange under the influence of mechanical or thermal effects. These forces are of several strengths, the weakest being van der Waals, then those due to dipole interaction, hydrogen bonding, and ionic salt type valences. Only under a high stress are the latter forces rearranged.

With this concept of vulcanization, the known facts of both natural and synthetic rubber behavior can be explained. Some of these are:

1. Effect of acids and bases on the vulcanization reaction.
2. Action of accelerators.
3. Effect of metallic oxides and salts in vulcanization.
4. Quantity of combined sulfur required for optimum properties of various types of vulcanizates.

5. Reversion and reclaiming of rubber vulcanizates.
6. Bonding of rubber to metal.
7. Solubility changes on vulcanization.
8. Vulcanization of polychloroprene (Neoprene).
9. Vulcanization and properties of butadiene and isoprene polymers and copolymers.
10. Socalled history of memory effects of rubber vulcanizates.
11. Reversible and irreversible stress-strain temperature effects, including the large hysteresis loop of the first cycle of extension and retraction.
12. Reinforcement of rubber with carbon black and other fillers, which is believed to be due in part to dipole interaction between polar groups on the surface of the black and those of the vulcanized rubber. Thus, particle size, particle shape, and chemical nature of the surface become factors effecting carbon black reinforcement.

In conclusion, vulcanization may be considered as a process whereby the properties of rubber are changed toward the middle of the continuum of high molecular-weight linear polymers, at one end of which are polyisobutylene and crude rubber, with very weak intermolecular forces, and at the other end cellulose and nylon, with very strong intermolecular forces. Plasticization may be considered a reverse process to vulcanization, whereby strong intermolecular forces are weakened; for example, polyvinyl chloride is very rigid because of the strong intermolecular forces, but it becomes rubbery when these forces are weakened with plasticizers. There is one significant difference, however, in that the intermolecular forces are increased markedly at only a few points in vulcanization, whereas they are decreased uniformly along the whole chain in plasticization.

SUMMARY

x-Ray and stress-strain data have been obtained which indicate that accelerators and divalent metallic compounds, as well as sulfur, react with rubber molecules during vulcanization and become a part of the rubber vulcanizate. The vulcanization reaction was found to behave like a normal chemical reaction in solution, which is influenced by the temperature, solubilities of the reacting ingredients, relative strengths and concentrations of the acids present, pH, and chemical nature of the vulcanizing agent. On the basis of these results and the known characteristics of vulcanized rubber, the original hypothesis of Goodyear and the more recent conclusions of Midgley, Henne, and Shepard were developed into a theory of vulcanization which postulates that vulcanization is a process by which the intermolecular forces are increased through the introduction of polar groups, generally acidic in nature, into the rubber molecules. This is accomplished by the reaction of certain types of oxidizing agents with the alpha-methylene carbon atoms or double bonds. These intermolecular forces are further increased with soluble divalent metallic compounds by the formation of ionic valences between divalent metallic ions and polar acidic groups of the rubber vulcanizate. These divalent metallic ions may bridge the rubber molecules through ionic valences in the form of a salt. Intermolecular forces established during vulcanization give rigidity to the molecular structure, which retards plastic flow and crystallization of rubber molecules. They also are responsible for other characteristics of vulcanized rubber. The molecules in vulcanized rubber are presumably not joined by primary-valence bonds through sulfur or oxygen bridges, but retain their individual existence.

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REFERENCES

1 Guth and Mark, *Monatsh.* **65**, 93 (1934).
2 Kuhn, *Kolloid-Z.* **68**, 2 (1934).
3 Wall, *J. Chem. Physics* **10**, 485 (1942).
4 Goodyear, U. S. patent 3633 (1844).
5 Henriques, *Chem.-Ztg.* **17**, 634 (1893); **18**, 701, 1155 (1894).
6 Weber, *Z. angew. Chem.* **7**, 112, 142 (1894); *J. Soc. Chem. Ind.* **13**, 11 (1894).
7 Kindscher, in Memmler, "The Science of Rubber", translated by Dunbrook and Morris, New York, **1934**, p. 270.
8 Williams, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, Chap. 6.
9 Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
10 Le Bras and Compagnon, *Chim. & ind.* **46**, 291 (1941).
11 Van Amerongen and Houwink, *J. prakt. Chem.* **161**, 261 (1943).
12 Midgley, Henne and Shepard, *J. Am. Chem. Soc.* **56**, 1156 (1934).
13 Williams, *Proc. Rubber Tech. Conf. London*, **1939**, p. 304.
14 Clark, Le Tourneau and Ball, *Ind. Eng. Chem.* **35**, 198 (1943).
15 Williams, *Ind. Eng. Chem.* **26**, 1190 (1934); *Proc. Rubber Tech. Conf. London*, **1938**, p. 304.
16 Williams, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, Chap. 6; *Proc. Rubber Tech. Conf. London*, **1938**, p. 304.
17 Williams, *Ind. Eng. Chem.* **26**, 1190 (1934).
18 Roth and Wood, *J. Applied Physics* **15**, 749, 781 (1944).
19 Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935); RUBBER CHEM. TECH. **8**, 319 (1935).
20 Holt, *Ind. Eng. Chem.* **23**, 1471 (1931).
21 Van Dalfsen, *Arch. Rubbercultuur* **24**, 598 (1940); RUBBER CHEM. TECH. **16**, 318 (1943).
22 Blake, *Ind. Eng. Chem.* **22**, 737 (1930); Boggs and Blake, *Ind. Eng. Chem.* **22**, 748 (1930).
23 Wistinghausen, *Kautschuk* **5**, 57, 75 (1929).
24 Jones and Depew, *Ind. Eng. Chem.* **23**, 1467 (1931); Depew, *Ind. Eng. Chem.* **24**, 565 (1932); Jones, *Ind. Eng. Chem.* **25**, 1009 (1933).
25 Cotton and Westhead, *Trans. Inst. Rubber Ind.* **13**, 230 (1937).
26 Armstrong, Little and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).
27 Newton, *Ind. Eng. Chem.* **34**, 374 (1942).
28 Newton and Willson, *Ind. Eng. Chem.* **34**, 378 (1942).
29 Sears, *J. Applied Physics* **12**, 35 (1941).
30 Sheppard and Sutherland, *Trans. Faraday Soc.* **41**, 261 (1945).
31 Farmer and Michael, *J. Chem. Soc.* **1942**, p. 513.
32 Farmer, in "Advances in Colloid Science", edited by Mark and Whitby, New York, **1946**, Vol. 2, p. 356.

THE COMBINED ACTION OF MALEIC *N*-METHYLIMIDE AND *p*-BROMOBENZOYL PEROXIDE ON NATURAL RUBBER *

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It is already known that natural rubber is capable of combining, under certain conditions, with various unsaturated compounds. Bacon and Farmer[1], for example, have fixed maleic anhydride on rubber in solution in the presence of benzoyl peroxide. This reaction has been applied likewise to acrylic acid, to acrylonitrile[2] and to methacrylonitrile[3]. Bacon and Farmer carried out the reaction with solutions of rubber which were refluxed for 18 hours, without, however, attempting to avoid the extraneous effect of atmospheric oxygen.

The present author was, therefore, prompted to carry out the reaction protected from air in sealed tubes into which the solvent was introduced by distillation in a vacuum according to a technique based on that employed by Moureu and Dufraisse[4] in their studies of autoxidation.

In an effort to explain the mechanism of the reactions, maleic *N*-methylimide was chosen as the unsaturated reagent in the reaction and *p*-bromobenzoyl peroxide as the catalyst. These two compounds, in virtue of the nitrogen atoms and bromine atom in their respective molecules, made it possible to determine by analysis what became of them as a result of the reaction.

It was observed first of all that, depending on the conditions of the reaction, particularly the temperature and the concentration of rubber in the solvent, gels were formed in some cases and soluble products in other cases. Thus, below 120–130° C, a gel was formed whatever the temperature, and whatever the concentration of the rubber, provided only that the concentration was greater than 3–4 per cent. On the contrary, when the temperature was higher than 120–130° C, and the concentration was not above 3–4 per cent, soluble products were obtained.

An additional clue to the structure of these products can be obtained by determining their iodine numbers. To do this, soluble products must be analyzed, and for this reason the present systematic investigation was carried out by heating 3 per cent solutions of rubber in benzene for 15 hours at 130° C. The initial concentration of *p*-bromobenzoyl peroxide was varied from 0.0034 to 0.34 molecule per C_5H_8 group of the rubber; the initial concentration of the maleic *N*-methylimide from 0.1 to 1 molecule per C_5H_8 group. After being purified and dried, the products were analyzed, with the following results.

The presence of bromine in the addition products shows that the peroxide does not play the part of a true catalyst, but that it apparently initiates reactions of free radicals in the chain. If it is assumed that its molecule breaks up into two radicals, $p\text{-BrC}_6H_4COO-$, the extent of fixation of these radicals on the rubber would be approximately 50 per cent.

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The proportion of maleic N-methylimide which was fixed on the rubber depended directly on the proportion originally added (see Figure 1), that is, it was practically proportional to the square root of the original content of p-bromobenzoyl peroxide when this was less than 0.01 molecule per C_5H_8 group (see Figure 2).

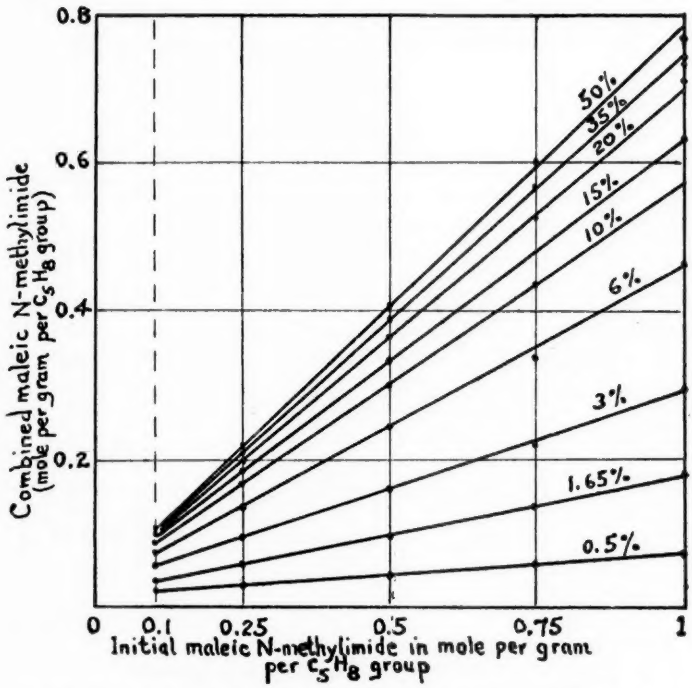

FIG. 1.—Combined maleic N-methylimide as a function of the initial amount of maleic N-methylimide with different initial amounts of p-bromobenzoyl peroxide (shown on the graphs as percentage).

Determinations of unsaturation with respect to the rubber did not give results which could be interpreted with any great certainty[5]. However, the loss of unsaturation varied in the same sense as the fixation of the brominated radicals formed by decomposition of the p-bromobenzoyl peroxide, and all evidence leads necessarily to the conclusion that the loss of unsaturation can be attributed almost exclusively to the action of the peroxide. Whatever the true explanation, the values found for the unsaturation indicate that almost all of the maleic N-methylimide is fixed elsewhere than at the double bonds of the rubber. It is probable that fixation occurs on the α-methylenic carbon atoms, in accordance with the substituting addition mechanism described by Alder[6] for simple olefins and extended to rubber by Farmer[7].

Finally it should be pointed out that the appearance of the compounds soluble in benzene is identical to that of the products prepared by Bacon and Farmer with maleic anhydride and benzoyl peroxide. Dependent on the content of maleic N-methylimide, a series of products passing from rubberlike to inelastic fibrous substances and then to white powders was obtained. The white powders theoretically can contain as high as 62 per cent of maleic

N-methylimide by weight, *i.e.*, 1 molecule of maleic *N*-methylimide per C_5H_8 group. But even when heating was continued for 16 hours, the highest percentage reached was 52.5, in which case the powder obtained was soluble in acetone, probably because of the large number of =CO groups present in the addition compound.

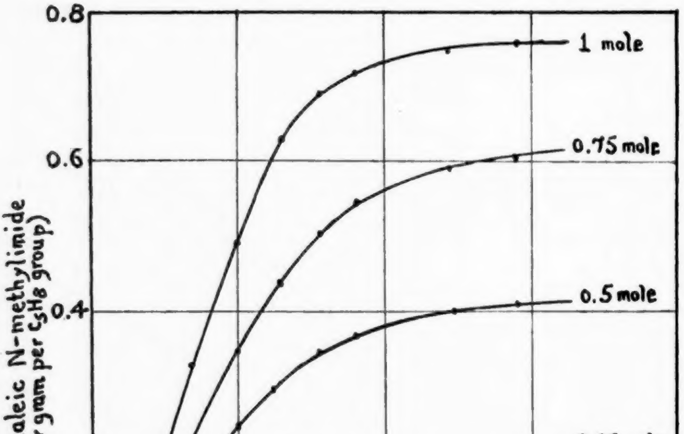

FIG. 2.—Combined maleic *N*-methylimide as a function of the square root of the initial amount of *p*-bromobenzoyl peroxide with different initial amounts of maleic *N*-methylimide (shown on the graphs in terms of moles).

REFERENCES

[1] Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, **1938**, p. 256; RUBBER CHEM. TECH. **12**, 200 (1939).
[2] Compagnon and Delalande, *Rev. gen. caoutchouc* **20**, 133 (1943); RUBBER CHEM. TECH. **20**, 689 (1947).
[3] Le Bras and Compagnon, *Bull. soc. chim.* **11**, 553 (1944); RUBBER CHEM. TECH. **20**, 938 (1947).
[4] Moureu and Dufraisse, *Inst. intern. chim. Solvay 2° Conseil de Chimie*, **1925**, p. 578.
[5] The method of Wijs gives excellent results with rubber which has not been modified, but it seems possible that the complicated structure of the molecule obstructs the total fixation of iodine on the double bonds.
[6] Alder, *Ber.* **76**, 27 (1943).
[7] Farmer, *Trans. Faraday Soc.* **38**, 349 (1942); RUBBER CHEM. TECH. **15**, 765 (1942); *Endeavour* **3**, 72 (1944).

THE PHOTOELASTIC PROPERTIES OF RUBBER.

I. THEORY OF THE OPTICAL PROPERTIES OF STRAINED RUBBER *

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In this paper the optical properties of vulcanized rubber subjected to the most general type of homogeneous strain are examined theoretically, on the basis of a molecular-network model essentially similar to that already successfully applied by a number of authors in the determination of the mechanical properties of vulcanized rubber.

The foundations of the optical theory have been laid by Kuhn and Grün[1], who considered first the optical properties of a statistically-kinked long-chain molecule composed of optically anisotropic links. They next examined the problem of a network of such molecules subjected to a simple elongation, obtaining formulas for the variation of birefringence with elongation. They showed that the stretched rubber could be characterized by two principal refractive indices, corresponding to directions of polarization parallel and perpendicular to the direction of extension, respectively. It is, therefore, optically equivalent to a uniaxial crystal.

In the more general case of a deformation described by three different extensions in three mutually perpendicular directions (pure homogeneous strain), we may anticipate that the optical properties correspond to those of a crystal not possessing axial symmetry, *i.e.*, a biaxial crystal. Such a crystal has three principal refractive indices, corresponding to three mutually perpendicular directions of the electric vector of light rays propagated in it. These three principal refractive indices form the principal axes of the index ellipsoid, by which the refractive index for any other direction of electric vector is determined. From general considerations we may expect the principal axes of the index ellipsoid in strained rubber to have the same directions as the principal axes of the strain ellipsoid.

OPTICAL PROPERTIES OF STATISTICALLY-KINKED MOLECULE

Before proceeding to the general problem, it seems desirable that we review briefly the treatment of the single molecular chain, as given by Kuhn and Grün[1].

In this treatment the actual chain is replaced by an idealized chain of n universally-jointed, randomly-oriented links, each of length l. The links are assumed to be optically anisotropic and characterized by polarizabilities[2] α_1 along, and α_2 at right angles to their length.

To determine the principal polarizabilities of the chain and their dependence on the distance between its ends, we must know the angular distribution of the individual links corresponding to a given distance between the ends.

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The solution of this problem has been worked out by Kuhn and Grün, and is represented by the formula:

$$dn = e^{\alpha}e^{\beta \cos \theta} \cdot \tfrac{1}{2} \sin \theta d\theta \tag{1}$$

in which dn represents the number of links making an angle between θ and $\theta + d\theta$ to the line joining the ends of the chain. α and β are constants whose values depend on the distance r between the ends of the chain, and are given by the relations:

$$\beta = L^{-1} (r/nl) \tag{1a}$$

and

$$\alpha = n\beta/\sinh \beta \tag{1b}$$

The function L^{-1} in (1a) is the inverse Langevin function. Alternatively we may write:

$$r/nl = L(\beta) = \coth \beta - 1/\beta \tag{1c}$$

where L is the Langevin function.

We now consider the polarizability of the whole chain for the directions of the applied field, namely (1) parallel to the line joining the ends of the chain, and (2) at right angles to the line joining the ends of the chain.

Suppose the line joining the ends to coincide with the axis OX of a rectangular coördinate system. Let any given link of the chain make an angle θ with OX, and suppose that the plane containing the angle θ makes an angle ϕ with the plane YOX. The polarizabilities of this link, for fields, respectively, along OX and OY are then given by the relations:

$$\left.\begin{aligned} \alpha_x &= \alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta \\ \alpha_y &= (\alpha_1 - \alpha_2) \sin^2 \theta \cos^2 \phi + \alpha_2 \end{aligned}\right\} \tag{2}$$

and the corresponding total polarizabilities of the chain, being the sum of the polarizabilities of the single links, will be:

$$\begin{aligned} \gamma_1 &= \int \alpha_x dn \\ \gamma_2 &= \int \alpha_y dn \end{aligned} \tag{3}$$

The number of links at angles between θ and $\theta + d\theta$ and ϕ and $\phi + d\phi$ is from (1):

$$dn\theta, \phi = e^{\alpha}e^{\beta \cos \theta} \cdot \tfrac{1}{2} \sin \theta \cdot d\theta \frac{d\phi}{2\pi} \tag{4}$$

since all values of ϕ are equally probable. Introducing this distribution into (3) gives, for the polarizabilities of the chain parallel and perpendicular, respectively, to the line joining its ends,

$$\begin{aligned} \gamma_1 &= \int\int e^{\alpha}e^{\beta \cos \theta} \cdot \frac{1}{4\pi} \sin \theta d\theta d\phi (\alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta) \\ \gamma_2 &= \int\int e^{\alpha}e^{\beta \cos \theta} \cdot \frac{1}{4\pi} \sin \theta d\theta d\phi [(\alpha_1 - \alpha_2) \sin \theta \cos^2 \phi + \alpha_2] \end{aligned} \tag{5}$$

which on integration yield the result:

$$\left.\begin{aligned}\gamma_1 &= n\left[\alpha_1 - (\alpha_1 - \alpha_2)\frac{2r/nl}{L^{-1}(r/nl)}\right]\\ \gamma_2 &= n\left[\alpha_2 + (\alpha_1 - \alpha_2)\frac{r/nl}{L^{-1}(r/nl)}\right]\end{aligned}\right\} \tag{6}$$

for and, the difference of the two principal polarizabilities:

$$\gamma_1 - \gamma_2 = n(\alpha_1 - \alpha_2)\left(1 - \frac{3r/nl}{L^{-1}(r/nl)}\right) \tag{7}$$

Equations (6) and (7) may be written in the expanded form:

$$\left.\begin{aligned}\gamma_1 &= \frac{n}{3}(\alpha_1 + 2\alpha_2) + n(\alpha_1 - \alpha_2)\left[\frac{2}{5}\left(\frac{r}{nl}\right)^2 + \frac{24}{175}\left(\frac{r}{nl}\right)^4 + \frac{72}{875}\left(\frac{r}{nl}\right)^6 + \cdots\right]\\ \gamma_2 &= \frac{n}{3}(\alpha_1 + 2\alpha_2) - n(\alpha_1 - \alpha_2)\left[\frac{1}{5}\left(\frac{r}{nl}\right)^2 + \frac{12}{175}\left(\frac{r}{nl}\right)^4 + \frac{36}{875}\left(\frac{r}{nl}\right)^6 + \cdots\right]\end{aligned}\right\} \tag{6a}$$

$$\gamma_1 - \gamma_2 = n(\alpha_1 - \alpha_2)\left[\frac{3}{5}\left(\frac{r}{nl}\right)^2 + \frac{36}{175}\left(\frac{r}{nl}\right)^4 + \frac{108}{875}\left(\frac{r}{nl}\right)^6 + \cdots\right] \tag{7a}$$

From the expanded form (7a) it is seen that, if r is not too large, the anisotropy of the chain is proportional to r^2. Moreover, if the chain is free from external restraint, its average length is given by $r^2 = nl^2$; hence its average anisotropy is:

$$\gamma_1 - \gamma_2 \simeq \tfrac{3}{5}(\alpha_1 - \alpha_2)$$

i.e., $\frac{3}{5}$ of the anisotropy of a single link. The complete function (7) is plotted in Figure 1.

In the following treatment of the network it is assumed that the strain is not sufficiently large to cause any significant fraction of the total number of

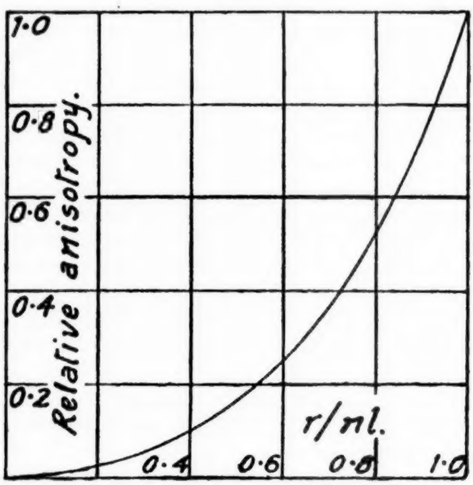

FIG. 1.

chains to assume lengths comparable with their fully-extended length nl, so powers of r/nl above the second, in the above expressions for the polarizabilities, may be neglected. (This assumption is equivalent to that made in the approximate theory of the mechanical properties of the network[3].) With this approximation, the chain polarizabilities reduce to the form:

$$\gamma_1 = C_1 + 2C_2r^2 \qquad \gamma_2 = C_1 - C_2r^2 \tag{6b}$$

in which the constants C_1 and C_2 have the values:

$$C_1 = \frac{n}{3}(\alpha_1 + 2\alpha_2) \qquad C_2 = \frac{\alpha_1 - \alpha_2}{5nl^2} \tag{8}$$

OPTICAL PROPERTIES OF THE NETWORK

Starting with a uniform spatial distribution of chain directions, the method employed by Kuhn and Grün in calculating the properties of the network involves the derivation of the distribution of length and direction of the chains in the deformed state of the network. The components of polarizability for each chain in directions parallel and perpendicular to the direction of extension are then written down, and the total polarizabilities in these two directions are obtained by integration over the whole assembly.

This direct method of approach appears to lead to formidable mathematical difficulties when applied to the more complex problem of the general homogeneous strain. Fortunately, however, these difficulties may be avoided by means of a somewhat less direct, but physically equivalent method, in which the necessity of integrating over all directions of the chains does not arise. This method will now be explained.

The network is assumed to contain N molecular chains, each consisting of n universally jointed links of length l. The junction points of the network are continually fluctuating in position on account of the random thermal motion of the chains, but for the calculation of the polarizabilities they are assumed to occupy their average positions. For simplicity, it is assumed initially that the distances between neighboring junction points, *i.e.*, the "displacement lengths" of the chains, in the undeformed rubber are all equal. (This restriction will be shown later to be unnecessary.) Finally, it is assumed that on deformation of the rubber the junction points move as if they were embedded in an elastic continuum. (This assumption is justified by James and Guth's analysis[4] of the mechanical behavior of a molecular network.)

In the unstrained rubber the displacement lengths (referred to subsequently simple as "lengths") of the assembly of chains may be represented by a set of vectors, assumed for the present to have equal lengths r. These vectors are distributed randomly in direction. Let us imagine that a set of three mutually perpendicular vectors is removed from this assembly, then a second set, then a third set, and so on. In this way it is seen that the original assembly of N vectors may be replaced by $N/3$ groups of three mutually perpendicular sets, each group being differently oriented with respect to a fixed coördinate system XYZ.

Considering for the moment only a single set of three mutually perpendicular chains, let us calculate the polarizabilities in the directions of the coördinate axes when the rubber is deformed.

The pure, homogeneous deformation is defined by stretches along OX, OY and OZ in the ratio λ_1, λ_2 and λ_3, respectively. Let (l_1, m_1, n_1), (l_2, m_2, n_2),

(l_3, m_3, n_3) be the direction cosines of the three chains in the unstrained rubber. The direction cosines for the first chain after the deformation are then given by:

$$l_1' = \frac{\lambda_1 l_1 r}{r_1}, \qquad m_1' = \frac{\lambda_2 m_1 r}{r_1}, \qquad n_1' = \frac{\lambda_3 n_1 r}{r_1} \tag{9}$$

and its length r_1 by:

$$r_1^2 = (\lambda_1^2 l_1^2 + \lambda_2^2 m_1^2 + \lambda_3^2 n_1^2) r^2 \tag{10}$$

with similar expressions for the other two chains. A chain making an angle θ with OX gives rise to a polarizability along OX of amount:

$$\beta = \gamma_1 \cos^2 \theta + \gamma_2 \sin^2 \theta$$

where γ_1 and γ_2 are the polarizabilities of the chain parallel and perpendicular, respectively, to its length. These polarizabilities are functions of r_1 given by Equation (6b). We therefore obtain, for the contribution of the first chain to the polarizability along OX:

$$\begin{aligned} \beta_{x_1} &= (C_1 + 2C_2 r_1^2) l_1'^2 + (C_1 - C_2 r_1^2)(1 - l_1'^2) \\ &= C_1 + C_2 r_1^2 (3 l_1'^2 - 1) \end{aligned}$$

From (9) $l_1'^2 r_1^2 = \lambda_1^2 l_1^2 r^2$ and r_1^2 is given by (10), hence:

$$\beta_{x_1} = C_1 + C_2 r^2 (2\lambda_1^2 l_1^2 - \lambda_2^2 m_1^2 - \lambda_3^2 n_1^2)$$

Similarly the contributions of the second and third chains to the polarizability along OX are:

$$\begin{aligned} \beta_{x_2} &= C_1 + C_2 r^2 (2\lambda_1^2 l_2^2 - \lambda_2^2 m_2^2 - \lambda_3^2 n_2^2) \\ \beta_{x_3} &= C_1 + C_2 r^2 (2\lambda_1^2 l_3^2 - \lambda_2^2 m_3^2 - \lambda_3^2 n_3^2) \end{aligned}$$

Remembering that $l_1^2 + l_2^2 + l_3^2 = 1$, etc., we obtain a total polarizability along OX of amount:

$$\beta_x = \beta_{x_1} + \beta_{x_2} + \beta_{x_3} = 3C_1 + C_2 r^2 (2\lambda_1^2 - \lambda_2^2 - \lambda_3^2)$$

The corresponding polarizabilities along OY and OZ are:

$$\left.\begin{aligned} \beta_y &= 3C_1 + C_2 r^2 (2\lambda_2^2 - \lambda_3^2 - \lambda_1^2) \\ \beta_z &= 3C_1 + C_2 r^2 (2\lambda_3^2 - \lambda_1^2 - \lambda_2^2) \end{aligned}\right\} \tag{11}$$

Equation (11) shows that the polarizabilities along OX, OY and OZ for a group of 3 mutually perpendicular chains are independent of their directions, since they do not contain the direction cosines. The polarizabilities depend, however, on r, the initial length of the chains and on the 3 principal extensions λ_1, λ_2 and λ_3

The advantage of the present method over the more direct method of Kuhn and Grün[1] will now be apparent. By choosing a suitable group of 3 chains, we have been able to obtain resultant polarizabilities which are independent of their original direction and thus to avoid the necessity of integrating over all directions. The total polarizabilities are obtained simply by multiplying by the number of groups of three chains in the network.

If instead of all the chains having the same initial length r, they have a distribution of lengths, such that N_a have the length r_a, N_b the length r_b, N_P the length r_P, etc., then, provided that N_a, $N_b \cdots N_P \cdots$ are large number, we may assume that the separate groups of vectors r_a, $r_b \cdots r_P$ each form a randomly oriented assembly, and may be separately divided into subgroups of 3

mutually perpendicular vectors for which the results represented by Equation (11) apply. For the whole assembly, therefore, the total polarizability per unit volume in the direction OX is:

$$\left.\begin{aligned} P_x = \Sigma\beta_x &= \Sigma N_p C_1 + \tfrac{1}{3}C_2 \Sigma N_p r_p^2(2\lambda_1^2 - \lambda_2^2 - \lambda_3^2) \\ &= N[C_1 + \tfrac{1}{3}C_2 \overline{r^2}(2\lambda_1^2 - \lambda_2^2 - \lambda_3^2) \end{aligned}\right\} \quad (12)$$

where $\overline{r^2}$ is the mean value of r^2.

If we assume that in the unstrained rubber the chains have the same average length as they would have if they were not attached to the network, we may write $\overline{r^2} = nl^2$. Inserting this value in (12) and expressing the constants C_1 and C_2 in their full forms (8), the resultant polarizabilities per unit volume in the directions OX, OY and OZ (assuming the volume to be unchanged on deformation) become:

$$\left.\begin{aligned} P_x &= N\left[\frac{n}{3}(\alpha_1 + 2\alpha_2) + \frac{1}{15}(\alpha_1 - \alpha_2)(2\lambda_1^2 - \lambda_2^2 - \lambda_3^2)\right] \\ P_y &= N\left[\frac{n}{3}(\alpha_1 + 2\alpha_2) + \frac{1}{15}(\alpha_1 - \alpha_2)(2\lambda_2^2 - \lambda_3^2 - \lambda_1^2)\right] \\ P_z &= N\left[\frac{n}{3}(\alpha_1 + 2\alpha_2) + \frac{1}{15}(\alpha_1 - \alpha_2)(2\lambda_3^2 - \lambda_1^2 - \lambda_2^2)\right] \end{aligned}\right\} \quad (13)$$

The principal indices of refraction may be obtained from the polarizabilities by making use of the well-known relation between refractive index (n) and polarizability per unit volume[5], *i.e.*:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \cdot P \quad (14)$$

Equations (13) with (14) provide a complete description of the optical properties of strained rubber in terms of the three principal extensions. When these extensions are all different, the principal refractive indices are also all different, and the rubber behaves like a biaxial crystal. If, on the other hand, two of the λ are equal as in the case of a unidirectional extension or compression, the equations reduce to the form given by Kuhn and Grün, and the system becomes comparable with a uniaxial crystal.

It is of interest to consider the behavior of light propagated along one of the axes of the index ellipsoid, say OZ. If the refractive indices for light polarized parallel to OX and OY, respectively, are n_1 and n_2, then, from (13) and (14):

$$\frac{n_1^2 - 1}{n_1^2 + 2} - \frac{n_2^2 - 1}{n_2^2 + 2} = \frac{4\pi N}{15}(\alpha_1 - \alpha_2)(\lambda_1^2 - \lambda_2^2) \quad (15)$$

If n_1 and n_2 do not differ greatly from the mean index $\bar{n}$, the following approximation is valid:

$$\frac{n_1^2 - 1}{n_1^2 + 2} - \frac{n_2^2 - 1}{n_2^2 + 2} \simeq \frac{6\bar{n}}{(\bar{n}^2 + 2)^2}(n_1 - n_2) \quad (16)$$

and therefore the birefringence for the direction of propagations OZ may be written:

$$n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} N(\alpha_1 - \alpha_2)(\lambda_1^2 - \lambda_2^2) \quad (15a)$$

i.e., the difference between any two of the principal refractive indices is proportional to the difference of the squares of the corresponding extension ratios.

THE RELATION BETWEEN BIREFRINGENCE AND STRESS

Methods of treating the mechanical properties of a network of molecular chains have been given by a number of authors, among whom may be mentioned in particular James and Guth[4], Wall[6] and Flory and Rehner[7]. Fundamentally, these different approaches have much in common, and the author has shown[8] that the treatments both of Wall and of Flory and Rehner lead to the same expression for the work of deformation in a homogeneous strain of the most general type.

It is a simple matter to confirm that an identical result is obtainable by means of the method used in this paper for the derivation of the optical properties of a network. For this purpose we write the entropy of a randomly-linked chain as a function of its length in the form given by Kuhn[9]:

$$s = c - \frac{3k}{2nl^2} \cdot r^2$$

Taking, as before, a set of 3 mutually perpendicular chains of initial length r and direction cosines (l_1, m_1, n_1), etc., whose lengths after the deformation defined by extension ratios λ_1, λ_2 and λ_3 are given by equations of the type (10), we find, for the entropy change on deformation:

$$-\frac{s' - s}{3k/2nl^2} = (\lambda_1^2 l_1^2 + \lambda_2^2 m_1^2 + \lambda_3^2 n_1^2)r^2 + (\lambda_1^2 l_2^2 + \lambda_2^2 m_2^2 + \lambda_3^2 n_2^2)r^2 + (\lambda_1^2 l_3^2 + \lambda_2^2 m_3^2 + \lambda_3^2 n_3^2)r^2 - 3r^2$$

or

$$-\frac{s' - s}{3k/2nl^2} = (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)r^2 \qquad (17)$$

Since this expression is independent of the direction cosines of the chains, we may use the same arguments as were employed in the foregoing optical treatment, and write, for the entropy change on deformation for the whole assembly of N chains, occupying unit volume:

$$\Delta S = -\frac{Nk}{2nl^2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)\overline{r^2} \qquad (18)$$

If now we put $\overline{r^2}$ the mean square length in the unstrained state equal to nl^2, the work of deformation $W(= -T\Delta S)$ becomes:

$$W = \tfrac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (19)$$

as previously derived by the other methods.

The subsequent calculation of the principal stresses from Equation (1a) has been dealt with elsewhere[3]. In particular it has been shown that the difference between any two of the 3 principal stresses, t_1, t_2 and t_3, may be expressed in terms of the corresponding strains; thus, for example:

$$t_1 - t_2 = NkT(\lambda_1^2 - \lambda_2^2) \qquad (20)$$

Comparing this expression with Equation (15a), we see that the difference between any two of the principal refractive indices is proportional to the differ-

ence between the corresponding principal stresses. The proportionality factor is a function only of the anisotropy of the chain link and the mean polarizability, *i.e.*, refractive index, of the medium, and is given by:

$$\left(\frac{n_1 - n_2}{t_1 - t_2}\right)_{\lambda_1\lambda_2\lambda_3\ \mathrm{const.}} = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} \cdot \frac{\alpha_1 - \alpha_2}{kT} \qquad (21)$$

Being independent of the number of links in the chain and the number of chains in the network, this constant should be a specific property of the type of rubber, and independent of the degree of vulcanization.

STRAINED SWOLLEN RUBBER

In this section the optical and mechanical properties of vulcanized rubber swollen by a low-molecular liquid are considered.

The swelling liquid is assumed to be optically isotropic. If v_r is the volume fraction of the rubber in the mixture, the number of chains per unit volume of the swollen rubber is v_rN, and their mean square length in the absence of mechanical deformation is increased from nl^2 to $nl^2/v_r^{2/3}$. The contributions to the polarizability per unit volume along the coördinate axes due to the network are, therefore, given by equations of the form:

$$P_x = Nv_r\left[\frac{n}{3}(\alpha_1 + 2\alpha_2) + \frac{1}{15}\cdot\frac{\alpha_1 - \alpha_2}{v_r^{2/3}}(2\lambda_1^2 - \lambda_2^2 - \lambda_3^2)\right] \qquad (22)$$

in place of (13), and the difference between any two of the principal refractive indices by:

$$n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} \cdot N(\alpha_1 - \alpha_2)v_r^{1/3}(\lambda_1^2 - \lambda_2^2) \qquad (23)$$

where $\bar{n}$ is now the mean refractive index for the mixture of rubber and liquid, and N is the number of chains per unit volume of the unswollen rubber.

Similarly the work of deformation per unit volume of the swollen rubber is:

$$W = \tfrac{1}{2}NkTv_r^{1/3}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (24)$$

From this equation it follows that the principal stresses decrease with swelling, in the ratio[10], $v_r^{1/3}$. Since this factor also occurs in the birefringence Equation (23) it is clear that the ratio of the birefringence to the difference of the principal stresses is still given by Equation (21). The relations between birefringence and stress are, therefore, unaffected by swelling, except in so far as the swelling liquid may alter the mean refractive index $\bar{n}$.

CONCLUSION

The foregoing results bring out certain simple relations between the optical properties and the mechanical properties of vulcanized rubber. The equations derived are valid only up to moderate strains, and do not apply when the strains begin to approach the limiting deformability of the network.

The treatment given above makes use of the concept of a chain of independently oriented statistical links. Although no actual molecular structure conforms exactly to this idealized model, the behavior of any flexible molecule approximates to that of the random chain in the region of small or moderate extensions. With this limitation, the theory should, therefore, be valid for all rubberlike materials.

ACKNOWLEDGMENT

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SUMMARY

From the consideration of vulcanized rubber as a network of randomly kinked molecular chains, the optical constants corresponding to the most general type of homogeneous strain are derived. Under such a strain the rubber is shown to acquire the properties of an optically biaxial crystal, characterized by three principal refractive indices in the directions of the principal axes of strain. For directions of light propagation parallel to one of the principal axes, the birefringence is shown to be a simple function of the principal extensions and is, moreover, proportional to the difference between the two corresponding principal stresses.

If the rubber is swollen with a liquid having the same refractive index as itself, the birefringence for a given state of strain varies inversely as the cube root of the swelling ratio, as do also the principal stresses.

REFERENCES

[1] Kuhn and Grün, *Kolloid-Z.* **101**, 248 (1942).
[2] Polarizability is the ratio of induced dipole moment to electric field strength.
[3] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943).
[4] James and Guth, *J. Chem. Physics* **11**, 455 (1943).
[5] Joos, "Theoretical Physics", **1934**, p. 434.
[6] Wall, *J. Chem. Physics* **10**, 485 (1942).
[7] Flory and Rehner, *J. Chem. Physics* **11**, 512, 521 (1943).
[8] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943); **42**, 83 (1946).
[9] Kuhn, *Kolloid-Z.* **76**, 258 (1936).
[0] Both James and Guth (see Reference no. 4) and Flory and Rehner (see Reference no. 7) have derived this result for the case of a unidirectional stretch.

II. DOUBLE REFRACTION AND CRYSTALLIZATION IN STRETCHED VULCANIZED RUBBER *

L. R. G. Treloar

In this paper experimental birefringence data for vulcanized rubber extended at a series of temperatures ranging from $-50°$ to $+100°$ C are presented. The principal objective was the separation of the birefringence due to crystallization from the genuine strain-birefringence, with a view to comparing the dependence of strain-birefringence on extension and on stress with the forms predicted by the theory given in the preceding paper. The effects produced by swelling the rubber with solvents before stretching are also examined.

In the case of a simple elongation, defined by the ratio α of the stretched to the unstretched length, the theoretical variation of the strain-birefringence with α, obtained by putting $\lambda_1 = \alpha$, $\lambda_2 = \alpha^{-\frac{1}{2}}$ in Equation (15a) of the preceding paper, is

$$n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} \cdot N(\alpha_1 - \alpha_2)(\alpha^2 - 1/\alpha) \tag{1}$$

where $\alpha_1 - \alpha_2$ represents the optical anisotropy of the equivalent statistical

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link of the chain molecule, and N is the number of chains per cc. The tension F referred to unit area of the unstrained cross-section, has the theoretical form:

$$F = NkT(\alpha - 1/\alpha^2) \tag{2}$$

The stress t referred to the actual section is αF, and the ratio of birefringence to stress, for a given value of α is given by the equation:

$$\left(\frac{n_1 - n_2}{t}\right)_\alpha = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} \cdot \frac{\alpha_1 - \alpha_2}{kT} \tag{3}$$

which is comparable with Equation (21) of the preceding paper.

EXPERIMENTAL

The vulcanized rubber used in these experiments was compounded in parts by weight according to the following formula:

Smoked sheet rubber	100
Sulfur	2
Zinc oxide	2
Benzothiazoyldisulfide	1
Stearic acid	0.5
Nonox	0.5

The extension was carried out with the apparatus described in an earlier publication[1], the tension being measured by the deflection of a flat steel spring with attached pointer. The birefringence was measured by using white light polarized in a plane making an angle of 45° with the direction of the extension, in conjunction with a Babinet compensator and analyzer at right angles to the polarizer. The elongation was measured with a travelling microscope focussed on two fiduciary lines on the test specimen distant 10 mm. apart. At each extension the elongation was measured first, then the birefringence, and finally the tension. The time involved was not controlled, but averaged about 3 minutes for the three measurements. The thickness of the specimen was obtained by weighing. For the experiments at temperatures above room temperature an air thermostat was employed. For lower temperatures the system was surrounded by a glass tube immersed in a suitable cooling mixture.

Two thicknesses of sheet were used. The thicker sheet (about 0.8 mm. thickness) was used where high extensions were not involved. Dumb-bell test-pieces were cut from this sheet. The thinner sheet (about 0.1 mm.) was employed for measurements involving the highest extensions. In these cases parallel test-pieces were used, the effect of nonuniform strain at the clamps being reduced by clamping the rubber in the stretched condition.

In a previous publication[2] the details of the birefringence measurement were discussed in connection with raw rubber. The birefringence B used in that paper was the path difference per mm. for sodium light. In the present work it is more convenient (for comparison with the theory) to convert this to difference of principal refractive indices by multiplying this quantity by the wavelength, *i.e.*, $n_1 - n_2 = B\lambda$.

HYSTERESIS EFFECTS

A typical birefringence-elongation curve, taken at 25° C, is reproduced in Figure 1(B), which shows the presence of a marked hysteresis loop on traversing

a cycle of extension and retraction. The presence of a hysteresis loop of this kind has been shown by the comparison of x-ray and optical observations by Triessin and Wittstadt[3] to be correlated with changes in the state of crystallization in the rubber. Curve A in Figure 2 shows a corresponding hysteresis loop in the tension curve. This effect is due to the tendency of the oriented crystalline state to maintain itself when the tension is reduced.

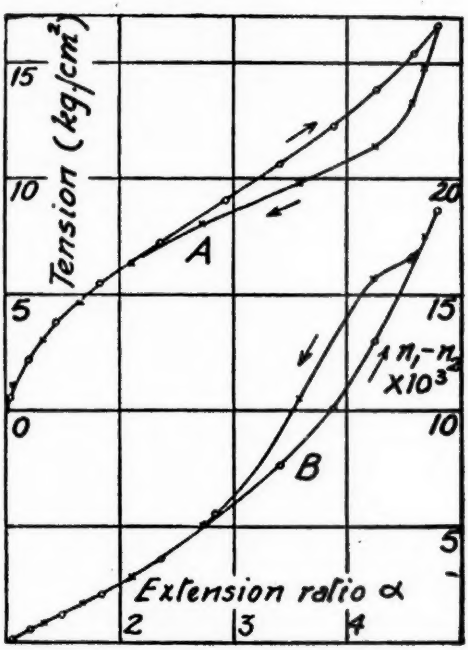

FIG. 1.—Hysteresis phenomena as shown by tension (A) and birefringence (B) in vulcanized rubber at 25° C.

When the birefringence is plotted against the applied stress (Figure 2) the two hysteresis effects are added together to produce a still larger loop. Raising the temperature successively to 50° and 75° (Figure 2) leads first to a reduction and then to the complete disappearance of the hysteresis, which must be due to a successive reduction in the amount of crystallization.

At the highest temperature the birefringence-stress relation approximates to the theoretical linear form represented by Equation (3). The slight curvature is probably due mainly to the departure of the tension curve from the theoretical form (2) at high extensions, as will be evident later. At the lower temperatures the theoretical relation is followed only at small extensions; thereafter the predominant effects of crystallization lead to large irreversible departures from this form.

TEMPERATURE VARIATION OF STRESS AND BIREFRINGENCE

In a more extensive examination of the dependence of stress and birefringence on temperature, observations were made from the lowest extensions up to the breaking point at temperatures ranging from -50 to $+100°$ C. The

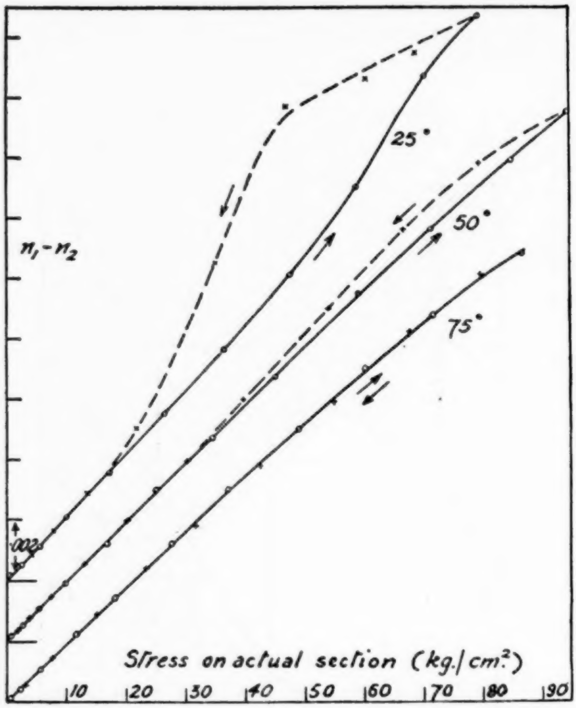

FIG. 2.—Hysteresis phenomena as shown by plot of birefringence against stress. Circles-stress increasing; crosses-stress decreasing.

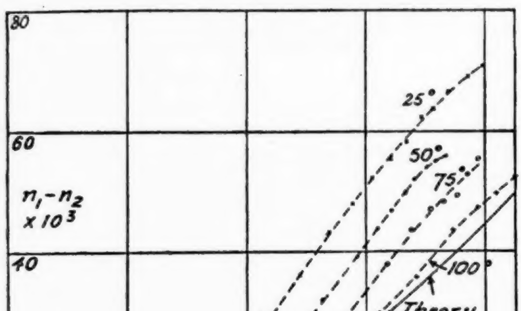

FIG. 3.—Comparison of birefringence-elongation curves at various temperatures with theoretical form (1).

birefringence data (Figures 3 and 4) shows a fairly close agreement with the approximate theoretical form of dependence on extension ratio (Equation 1) at the lower extensions, but diverge from this form at higher extensions. Apart from the $-50°$ curve, which is anomalous, the range over which the experimental data fit the theoretical curve becomes greater with each increase in temperature, indicating a progressive increase in the extension required for the appearance of crystallization. The 100° curve suggests that even at this temperature some crystallization may be present at the highest extensions; this is supported by the observation of a strong hysteresis loop when the extension was stopped just short of the breaking point and reversed. The degree of agreement of the birefringence-elongation curves (up to the point where crystallization begins) with the theoretical relation (Equation 1) is closer than might have been expected, in view of the approximate nature of the theoretical formula, and must be regarded as somewhat fortuitous.

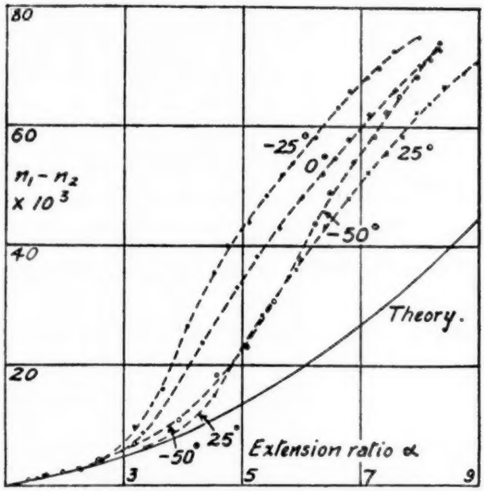

Fig. 4.—Comparison of birefringence-elongation curves at various temperatures with theoretical form (1).

From the observations of Bekkedahl[4] and others it is known that crystallization in unstretched rubber takes place most rapidly in the temperature range -35 to $-15°$ C, but not at all at a temperature of $-50°$ C. It is not surprising, therefore, that in the present experiments crystallization apparently takes place less readily at $-50°$ C than at $-25°$ C. This anomalous behavior is shown very clearly in Figure 7, which represents the birefringence-stress relation for selected temperatures; at $-25°$ C and $+25°$ C, crystallization is revealed by a sudden increase in birefringence at a relatively low stress, but at $-50°$ C, as at $+100°$ C, no such effect is observed.

A parallel effect of crystallization is seen in the stress-strain curves (Figures 5 and 6). As the maximum extensibility of the molecular network is approached, the stress-strain curve shows a strong upward curvature. The extensibility is a function of the length of molecular chain between junction points. In an ideal rubber the only effective junction points are the permanent cross-linkages between molecules produced in vulcanization. In a rubber,

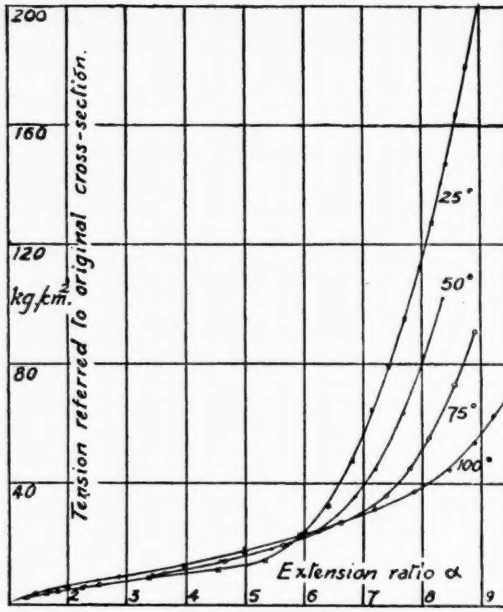

FIG. 5.—Tension-elongation curves at various temperatures.

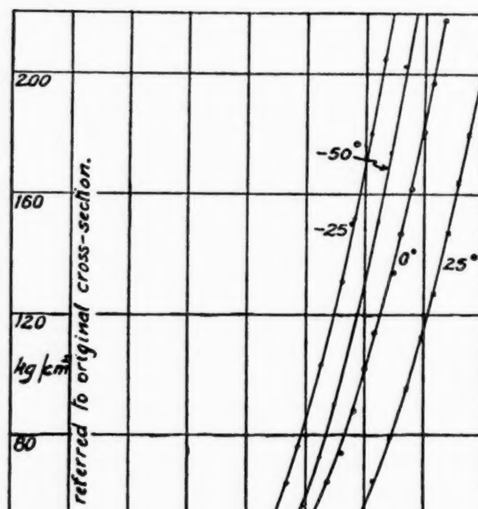

FIG. 6.—Tension-elongation curves at various temperatures.

mechanical entanglements may give rise to temporary junction points, which, by reducing the average length of free chain, reduce the overall extensibility. Crystallization acts in the same way, since crystallization has the effect of providing additional cross-linkages between the molecules. As the temperature is lowered, both these effects are normally increased, and the upward bend of the stress-strain curve moves to a lower extension. This is seen to be true for all the curves from +100° to −25° C. At −50°, however, the sequence is reversed, and the extensibility again increases, owing to the reduction in crystallization, which more than compensates for the increased mechanical cohesion. In connection with the birefringence-stress data, it should be noted that the conditions of the experiment did not give genuine equilibrium stress-strain data, and to this extent are open to criticism. In the present work, however, the object was mainly to obtain a general picture of the phenomena of birefringence rather than to explore the details in a quantitatively accurate manner.

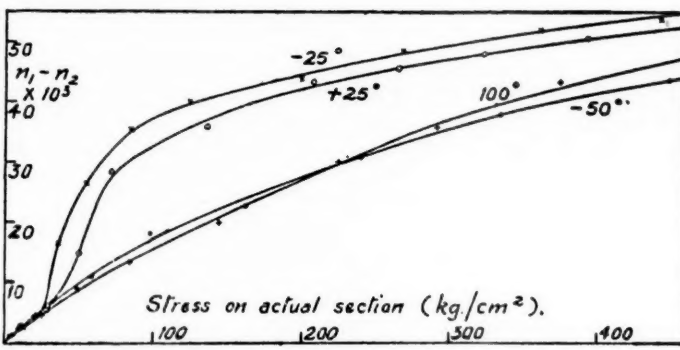

FIG. 7.—Birefringence-stress curves at selected temperatures.

The downward curvature of the birefringence-stress curves at higher values of α is connected mainly with the departure of the stress-strain curves from the simple theoretical form, due to the non-Gaussian form of the distribution function for molecular lengths[5].

THE MAXIMUM BIREFRINGENCE

The observations in the preceding paragraph suggest that entanglements may be more numerous at the lower temperatures. It would seem to follow from this that if stretching were carried out at a comparatively high temperature, and crystallization subsequently completed at a lower temperature, a higher proportion of crystalline material might be obtained than by stretching at the lower temperature. This expectation was borne out experimentally, though the effect was not very marked. The maximum birefringence was obtained by stretching to a high extension at room temperature (21° C), subsequently cooling to −25° C, and then increasing the extension until breaking occurred. In this way a birefringence $n_1 - n_2$ of 0.0827 at $\alpha = 9.12$ was obtained, compared with 0.0752 at $\alpha = 7.99$ for continuous extension at −25° C. The corresponding stresses were about the same for both *i.e.*, 2400 and 2100 kg. per sq. cm., respectively (on the actual section). Still higher birefringences were obtained with unvulcanized rubber (crepe film from solution) by a similar

process. The highest figure was obtained by stretching at 0° C, with subsequent cooling to −25° and further stretching. This gave $n_1 - n_2 = 0.0945$ at $\alpha = 10.1$, the stress being 1200 kg. per sq. cm. Unfortunately it is not possible to say how nearly complete crystallization was approached in these experiments, and it is probable that, if held extended for a considerable time at a low temperature, the samples might have shown further increases in birefringence. They do, however, enable a lower limit to be set up to the birefringence of the rubber crystal.

It is interesting to compare the maximum birefringence obtained experimentally with the maximum theoretical birefringence, that is, the birefringence corresponding to a complete orientation of all the chain links parallel to a fixed direction. This may be estimated from a knowledge of $\alpha_1 - \alpha_2$, the anisotropy of the chain link, which is itself determined by the stress-optical coefficient, according to Equation (3). Experimentally, at 25° C, the plot of birefringence against stress in the region of low elongation gives $(n_1 - n_2) = 2.33 \cdot 10^{-4}t$. Taking $\bar{n}$, the mean refractive index to be 1.525, we obtain, from Equation (3):

$$\alpha_1 - \alpha_2 = 5.65 \cdot 10^{-24}$$

The difficulty now arises of interpreting the meaning of the statistical chain link. From a theoretical treatment of the isoprene structure, the author[6] has shown that the polyisoprene chain is statistically identical with a random universally-jointed chain in which each link replaces 1.42 isoprene units[7].

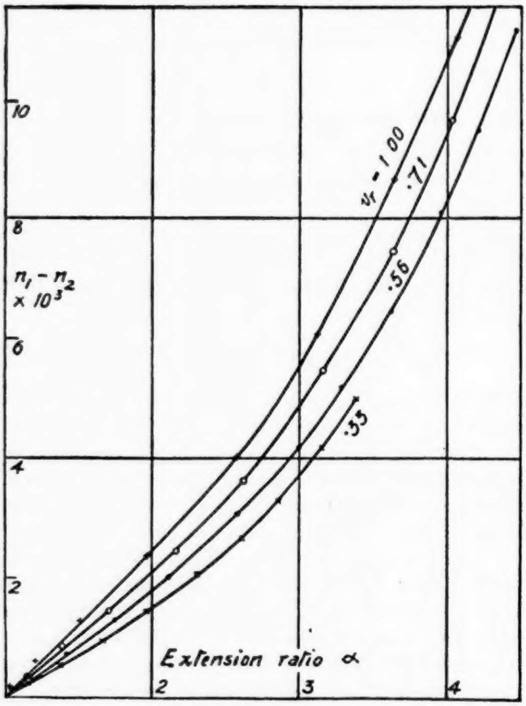

FIG. 8.—Birefringence-elongation curves for rubber swollen with squalene. v_r = volume fraction of rubber.

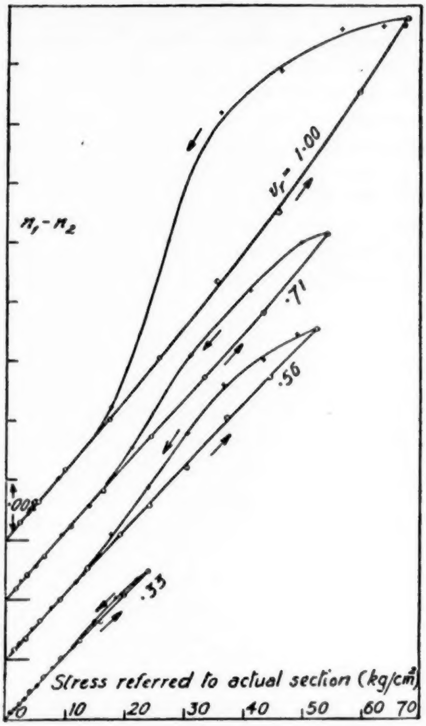

FIG. 9.—Birefringence-stress curves for rubber swollen with squalene. v_r = volume fraction of rubber.

This result cannot be accurate, since it assumes perfect freedom of rotation about single bonds and neglects the volume occupied by the atoms. However, we may take it as an approximate basis for calculating the effective number of statistical chain links in the rubber. The number of isoprene units per cc. is 8.18×10^{21}, hence on this basis the number of equivalent random links per cc. is $8.18 \times 10^{21}/1.42 = 5.75 \times 10^{21}$. If all these links are parallel, the resultant difference of polarizability per cc. of rubber will be:

$$5.75 \times 10^{21}(\alpha_1 - \alpha_2) = 0.0325,$$

giving

$$n_1 - n_2 = \frac{(n^2 + 2)^2}{6n} \cdot \frac{4\pi}{3} \cdot (0.0325) = 0.28$$

This is about three times the highest experimentally observed birefringence (0.0945). The discrepancy is probably due mainly to the uncertainty in the assignment of the number of effective random links in the polyisoprene chain. However, the general agreement in order of magnitude provides a useful check on the basic correctness of the theory.

BIREFRINGENCE IN SWOLLEN RUBBER

For the experiments with swollen rubbers the sample was surrounded with a tube dipping into a cup of mercury to prevent escape of vapor. The upper

clamp was connected to the tension-measuring spring by means of a wire passing through a short length of capillary tubing. Diffusion of vapor through this aperture was not fast enough to be noticeable in the course of an experiment. The amount of swelling liquid present was calculated from the change in length of the unstretched sample.

The relation between birefringence and extension for rubber swollen with squalene ($C_{30}H_{50}$) up to about three times its original volume is shown in Figure 8. Neglecting the effect of the very small difference in refractive index of squalene and rubber (1.497 against 1.525) on the mean refractive index of the mixture, the birefringence should fall with swelling in proportion to $v_r^{\frac{1}{3}}$ (Equation (23) of preceding paper). Table I gives the observed values of

TABLE I

v_r	$n_1 - n_2$ at $\alpha = 2$	$v_r^{\frac{1}{3}}$	$\frac{n_1 - n_2}{v_r^{\frac{1}{3}}}$	$\frac{n_1 - n_2}{t}$
1.00	$2.45 \cdot 10^{-3}$	1.00	$2.45 \cdot 10^{-3}$	$2.33 \cdot 10^{-4}$
0.71	2.05	0.893	2.29	2.30
0.56	1.74	0.825	2.11	2.22
0.33	1.48	0.690	2.14	2.14

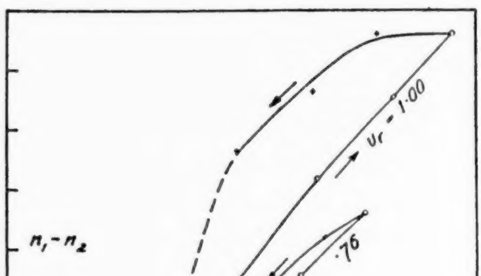

FIG. 10.—Birefringence-stress curves for rubber swollen with toluene. v_r = volume fraction of rubber.

$n_1 - n_2$ at $\alpha = 2.0$ and the corresponding values of the ratio $(n_1 - n_2)/v_r^{\frac{1}{3}}$. Evidently the birefringence falls rather more rapidly with swelling than is to be expected theoretically. From the curves for birefringence against stress (Figure 9) the ratio of birefringence to stress at low extensions was obtained. Theoretically this should be independent of the amount of swelling. The actual values are given in Table I. Birefringence stress data for rubber swollen with toluene, shown in Figure 10, yield very similar results. There is, however, an interesting difference in the magnitude of the hysteresis loops for the two liquids. It appears that crystallization (or, at least, irreversible orientation) persists to higher degrees of swelling with squalene than with toluene. Presumably the similarity of the squalene molecule to rubber enables it to conform to some extent with the local alignments of the rubber chains.

GENERAL CONCLUSION

From the experiments described in this paper, it is concluded that the molecular network theory gives a reasonably accurate description of the optical properties of stretched rubber in the dry and in the swollen state, so long as crystallization is avoided.

When crystallization is present, the departures from the theoretical form of the birefringence-elongation and birefringence-stress curves are apparent, and variations in birefringence give qualitative information about the variations in amount of crystallization. It does not seem possible, however, to obtain reliable quantitative estimates of the amount of crystallization corresponding to a given birefringence, firstly because the birefringence corresponding to 100 per cent crystallization is not known, and secondly, because the presence of crystallites, by altering the effective number of cross-links between molecules, alters the contribution of the strain-birefringence to the whole.

ACKNOWLEDGMENT

This work forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

SUMMARY

From an investigation of the variation of birefringence, with elongation in vulcanized rubber extended at temperatures ranging from $-50°$ to $+100°$ C, it is possible to distinguish the effects of crystallization from the true strain-birefringence. The latter agrees closely with theoretical expectations in its dependence on stress and on elongation. The data do not permit of a quantitative estimation of the relative amounts of crystalline material present under various conditions.

Experiments with stretched swollen rubber further confirm the theory and yield further evidence on the effects of crystallization.

REFERENCES

[1] Treloar, *Trans. Faraday Soc.* **37**, 84 (1941).
[2] Treloar, *Trans. Faraday Soc.* **36**, 538 (1940).
[3] Thiessen and Wittstadt, *Z. physik. Chem.* **41B**, 33 (1938).
[4] Bekkedahl, *Bur. Standards J. Research* **13**, 410 (1934).
[5] Treloar, *Trans. Faraday Soc.* **42**, 83 (1946).
[6] Treloar, *Trans. Faraday Soc.* **42**, 77 (1946).
[7] This is a mistake, which should be altered to "*each isoprene unit is equivalent to 1.42 random links*". The corresponding figure for the maximum birefringence should therefore be 0.56 (instead of 0.28), thus increasing the discrepancy between theory and experiment. [Subsequent communication from the author.]

EQUILIBRIUM PROPERTIES OF HIGH POLYMER SOLUTIONS AND GELS *

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The equilibrium between a polymer and a liquid is of fundamental importance in a number of problems of considerable practical as well as theoretical interest. As examples may be mentioned: (1) the choice of a solvent or plasticizer for a given polymer; (2) choice of a suitable polymer for use, *e.g.*, as a gasket in contact with specified liquids; (3) the combined solvent or swelling action of a mixture of liquids; (4) the effect of mechanical deformation, *e.g.*, compression, on the solvent resistance of a polymer; and (5) the separation of a polymer into fractions by the use of solvent-precipitant mixtures. It must be emphasized at the outset that in some of them other factors are involved, but these are not considered in the present paper. The basic assumption is made here that, given enough time, a system comprising polymer and liquid will reach a steady state, and that if two condensed phases are then present, they must be in true thermodynamic equilibrium. The disturbing influence of such time-dependent processes as degradation and plastic flow may, in certain practical cases, prevent the attainment of a steady state, but these possibilities require separate discussion. Within the limited space available, all that can be attempted is a brief outline of the general methods which have been used, illustrated by applying them to the first two of the above problems.

Thermodynamic formulation of the problem.—The function which will be used in discussing polymer–liquid equilibria is the Gibbs free energy of dilution of a polymer–liquid mixture by the pure liquid. It is denoted by ΔG_0 and defined as the increase in the Gibbs free energy G when 1 mole of liquid is transferred from a reservoir of pure liquid to an infinitely large bulk of a polymer–liquid mixture. Formally, if n_0 and n_r are the numbers of moles of liquid and of polymer in the mixture, at temperature T:

$$\Delta G_0 = \left(\frac{\partial G}{\partial n_0}\right)_{n_r, T} \tag{1}$$

Experimental measurements of ΔG_0 are based on observations of the vapor pressure p_0^m or other related properties of the mixture. If p_0^0 is the vapor pressure of the pure liquid, it may be shown[1] that:

$$\Delta G_0 = RT \ln (p_0^m/p_0^0) \tag{2}$$

The temperature dependence of ΔG_0 may be employed to calculate the heat ΔH_0 and entropy ΔS_0 of dilution; these are, respectively the increases in heat content H and entropy S accompanying the transfer of liquid as defined above.

* Reprinted from the *Journal of the Chemical Society*, 1947, pages 280–288.

Their relations to ΔG_0 are:

$$\Delta S_0 = (\partial \Delta G_0 / \partial T)_{n_0, n_r} \tag{3}$$

$$\Delta H_0 = \Delta G_0 + T\Delta S_0 \tag{4}$$

The condition for a polymer–liquid mixture to be in equilibrium with excess of liquid is simply $\Delta G_0 = 0$. If a swollen polymer is placed in contact with excess of liquid, further absorption of liquid will occur so long as the Gibbs free energy of the system is thereby decreased (ΔG_0 negative). If this is true at all concentrations of the mixture, the polymer and liquid in question will be miscible in all proportions. It is clear, therefore, that if some general expression could be found, giving ΔG_0 as a function of the composition of a polymer–liquid mixture, then equating this function to zero would give at once the composition of the mixture which would be in equilibrium with excess liquid. The next section describes some of the attempts which have been made to deduce such an expression.

The discussion so far has neglected the dispersion and solution of polymers in the liquid. This is only strictly justified in the case of polymers which are completely cross-linked into a network. Linear polymers have, in principle, a finite solubility in any liquid, and to define an equilibrium between polymer and liquid, it is necessary to specify the relative volumes of the two phases and the amount of polymer present in each. There are then two equilibrium conditions to be observed; namely, that the Gibbs free energy of the system shall be unaffected by transfer of small amounts of either liquid or polymer from one phase to the other. In practice it is found that, in almost all cases in which the polymer and liquid are not miscible in all proportions, the amount of polymer present in the liquid phase is so small that the liquid is virtually indistinguishable from pure liquid. The conditions under which two phases in equilibrium may both contain appreciable concentrations of polymer are so critical that they are encountered only when a range of molecular weights is present.

The extension of this formulation to systems containing more than one type of liquid is straightforward[2], and will not be discussed in detail. The two important problems are (1) the swelling of an insoluble polymer in mixtures, and (2) the fractionation of soluble polymers. In the former, differential absorption of the two liquids generally occurs, and two equations are required to define the complete composition of the swollen polymers at equilibrium. These are obtained from the conditions that the Gibbs free energy of the system must be unaffected by small transfers of either liquid from one phase to the other. The problem of fractionation is very complicated; even if the distribution of molecular weights is represented by a mixture of two only, there are four components distributed between the two phases, and therefore four conditions to be satisfied for equilibrium. These are readily written down, but are too complex to be of any practical value in their complete form.

The statistical approach to the probelm.—It has been shown above by thermodynamic reasoning that the problem of the equilibrium between a polymer and a liquid would be solved if an expression could be found for the dependence of the free energy of dilution on composition and temperature. The deduction of such an expression in terms of molecular properties of the polymer and liquid is a problem in statistical mechanics, and several attempts have been made to solve it[3]. The detailed description of these attempts is outside the scope of the present paper, and reference will be made only to the basic assumptions and the final results. To a first approximation the calculation of ΔG_0 may be

reduced to the two independent problems of finding expressions for ΔS_0 and ΔH_0. This approximation is valid if the mixing of polymer and liquid occurs in a completely random way.

Statistical derivations of ΔS_0 depend on Boltzmann's equation relating the entropy S of a state to its thermodynamic probability W:

$$S = \boldsymbol{k} \ln W \tag{5}$$

where $\boldsymbol{k}$ is Boltzmann's constant. Considering an assembly of polymer molecules and liquid molecules, if W_1, W_2, and W_3 are the respective probabilities of the polymer molecules alone, the liquid molecules alone, and a random mixture, then by Equation (5) the increase of entropy ΔS^m consequent upon mixing the components is given by:

$$\Delta S^m = \boldsymbol{k} \ln \left(\frac{W_3}{W_1 W_2} \right) \tag{6}$$

By analogy with Equation (1), ΔS_0 is then defined as $(\partial \Delta S^m / \partial n_0)_{n_r, T}$. To compute the probabilities, it is necessary to have a definite molecular model of the assembly; the one which has been used divides the space occupied by the assembly into a series of sites arranged in a regular lattice formation, defined by a fixed coördination number Z, *i.e.*, the number of nearest neighbors of any selected site. Each site is assumed to be capable of holding a single molecule of the liquid, and the spacing of the sites fixed by the known density of the liquid, "holes" being neglected. It is then imagined that the polymer can be divided into sections, each having the same volume as a molecule of liquid and, therefore, capable of occupying a single site. The flexibility of the polymer is taken into account by supposing that a molecule of polymer can be arranged on any set of sites, subject only to the restriction that adjacent sections of the polymer chain must occupy adjacent sites. The thermodynamic probability of the assembly is then obtained by computing the number of ways of arranging it on the lattice. In this way an expression is obtained for ΔS_0 in terms of the composition of the mixture, the number of sites (x) occupied by a single molecule of polymer, and the coördination number Z. It is clear from the description of the model that x is equal to the ratio between the molecular volumes of the polymer and liquid, and that the natural unit of composition is the volume fraction v_r of polymer, *i.e.*, the fraction of the total volume occupied by polymer.

The enumeration of the configurations of a polymer presents difficulties because of the necessity to exclude impossible arrangements in which two sections of a chain occupy the same site. Considering the process of adding a polymer molecule, section by section, to a partly filled lattice, the difficulty arises in estimating the probable number of sites available for the i'th section. The $(i - 1)$'th section is supposed to be in place; of its Z neighboring sites, one must be occupied by the $(i - 2)$'th section, but the probable number of the remaining $(Z - 1)$ which are vacant will clearly depend both on i and on the fraction of the total space which has already been filled. Flory[4] neglected the dependence on i, and obtained the final result in a remarkably simple form:

$$\Delta S_0 = -\boldsymbol{R} \{\ln (1 - v_r) + v_r(1 - 1/x)\} \tag{7}$$

ΔS_0 is seen to be independent of Z, while the dependence on x is only important when v_r is small enough to be comparable with $1/x$. Huggins[5] at-

tempted a partial correction for the dependence on i, and obtained finally:

$$\Delta S_0 = -\boldsymbol{R}\left\{\ln(1 - v_r) - \tfrac{1}{2}Z'(1 - 1/x)\ln\left(1 - \frac{2v_r}{Z'}\right)\right\} \tag{8}$$

where Z' is nearly identical with Z. Miller[6], by a different method of computation which will not be described here, obtained the very similar result:

$$\Delta S_0 = -\boldsymbol{R}\left[\ln(1 - v_r) - \tfrac{1}{2}Z\ln\left\{1 - \frac{2v_r}{Z}(1 - 1/x)\right\}\right] \tag{9}$$

It will be seen that Flory's result is identical with the asymptotic limit of (8) or (9) for large values of Z.

The heat of dilution has its origin in the exchange of partners between polymer and liquid during mixing. The transfer of a molecule of liquid from liquid to polymer may be imagined to take place in three steps, involving (1) evaporation of a molecule of liquid; (2) separation of the polymer chains so as to form a hole into which (3) the molecule of liquid is condensed. The first two steps require an absorption of energy in overcoming the cohesive forces of the liquid and the polymer; in the third, energy is recovered, and the heat of dilution is the algebraic sum of the three. A complete theory should predict the form of dependence of ΔH_0 on composition, and relate its magnitude to those of the intermolecular forces. The problem is very similar to that of calculating the heat of dilution ΔH_1 of a mixture of two liquids (1 and 2) by liquid 1; this has been discussed by van Laar[7], Hildebrand[8], Scatchard[9], and others. For random mixing of liquids it is easily shown that ΔH_1 should be proportional to the square of the concentration of species 2, but it is not at once clear in what units the concentration should be expressed. If the number of contacts is taken to be the important factor, then concentrations should be in mole fractions; if the effective surface of contact is the determining factor, volume fractions will be more appropriate. Experimental evidence[8] is strongly in favor of the latter, and in most treatments of polymer solutions, it has been assumed that the same relation would apply, *i.e.*:

$$\Delta H_0 = \alpha v_r^2 \tag{10}$$

where α is a constant. Although this type of expression will be used below, it must be pointed out that it is not strictly consistent with the model used in calculating ΔS_0. This would relate the heat of dilution to the number of polymer–liquid contacts, and (10) should be replaced by:

$$\Delta H_0 = \alpha'\left(\frac{qv_r}{1 + (q - 1)v_r}\right)^2 \tag{11}$$

where:

$$q = 1 - \frac{2}{Z} - \frac{2}{xZ} \tag{12}$$

Equations (10) and (11) are identical only in form in the physically meaningless case of $Z = \infty$.

To complete the calculation of ΔH_0, it is necessary to find an expression for α (or α'), and the only suggestion which has been made is to use the method applied by Hildebrand to liquid mixtures[10]. The energy required to separate all the molecules in 1 cc. of the liquid is the cohesive energy density of the liquid (E_{00}) given by:

$$E_{00} = (L_0 - RT)/V_0 \tag{13}$$

where L_0 is the molar latent heat of evaporation and V_0 the molar volume. Although Equation (13) cannot be applied to the polymer, it is perfectly logical to speak of its cohesive energy E_{rr}, to be estimated as described below. It is still necessary to know how the energy of a polymer–liquid contact is related to those of liquid–liquid and polymer–polymer contacts. The assumption of a geometric mean is likely to be valid when the forces involved are purely dispersion forces, and leads to the result:

$$\alpha = V_0(\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \tag{14}$$

Experimental evidence as to the usefulness of this relationship will be given in a later section

The simplest equation which can be obtained for the free energy of dilution results from combining Equations (4), (7), and (10), to give:

$$\Delta G_0 = RT\left\{\ln(1 - v_r) + v_r(1 - 1/x) + \frac{\alpha}{RT}v_r^2\right\} \tag{15}$$

If Equation (8) or (9) were used in place of (7), the final result would be almost identical, except that α/RT would be replaced by:

$$\mu = \mu_0 + \alpha/RT \tag{16}$$

where μ_0 is a function of Z but is nearly independent of v_r. This is the general form of the free-energy equation as deduced by the approximate method outlined. For convenience it may be written in two approximate forms:

(*a*) for dilute solution:

$$-\Delta G_0 = RT\left\{\frac{v_r}{x} + (\tfrac{1}{2} - \mu)v_r^2\right\} \tag{17}$$

(*b*) at higher concentrations ($v_r > 0.1$):

$$\Delta G_0 = RT\{\ln(1 - v_r) + v_r + \mu v_r^2\} \tag{18}$$

So far it has been assumed that the mixture is completely random, but it is clear that, unless the heat of dilution is zero, some configurations are energetically favored, and should accordingly be weighted in computing the configurations of the system. This has been done in different ways by Orr[11] and by Guggenheim[12], but the detailed results will not be quoted. The general conclusion is that a positive heat of dilution ($\Delta H_0 > 0$) results in nonrandom mixing, which increases ΔS_0 at low v_r and decreases it at high v_r. The effect, however, is very small, even when the heat of dilution is large, and seems unlikely to be important compared with the assumptions and approximations inherent in the method.

All methods of calculation used hitherto break down seriously for solutions sufficiently dilute for the polymer molecules to be individually dispersed, with relatively little overlap. In this region it is evident that, although the fraction of sites occupied by polymer is small, there is a relatively high probability of finding an occupied site adjacent to any selected site known to be occupied. In other words, the assembly may more properly be thought of as a dispersion of regions of fairly high concentration in a medium which elsewhere is pure liquid. This conclusion may be put in another way by saying that in an infinitely dilute solution there will still be a fairly large number of points at which sections of a polymer chain occupy adjacent sites. According to the method of calculation described above, in an infinitely dilute solution there

would be no polymer–polymer contacts. The present theory of dilute solutions is therefore definitely wrong, and two attempts to provide a new treatment may be mentioned. (1) Orr[13] has considered the arrangement of a single chain on a lattice, and has made tentative estimates of the number of polymer–polymer contacts to be expected, as a function of the heat of mixing. (2) Flory[14] has used the experimentally observed viscosity to make a rough estimate of the number of sites enclosed within the "envelope" of a single polymer molecule which, in the examples he quotes, is of the order of $50x$. On this basis he has estimated that the quadratic term in the expansion for ΔS_0 may be several times smaller than that given by Equation (17). There is no doubt of the reality of this discrepancy, but its quantitative treatment by purely statistical methods has not yet been accomplished.

One other factor which must be mentioned is the effect of cross-linking of the polymer. So far the polymer has been assumed linear, and it is clear that the introduction of cross-links between different polymer chains reduces the number of configurations of the system, and therefore diminishes ΔS_0. It is not proposed to describe here how this effect on ΔS_0 has been calculated; the result obtained[15] is:

$$\Delta S_0 = -\frac{R\rho_r V_0}{M_c} v_r^{-\frac{1}{3}} \tag{19}$$

where ρ_r is the density of the polymer, and M_c the "molecular weight" of the portion of the polymer between adjacent junction points. The free energy of dilution of a cross-linked polymer is therefore given by:

$$\Delta G_0 = RT \left\{ \ln (1 - v_r) + v_r + \mu v_r^2 + \frac{\rho_r V_0}{M_c} v_r^{-\frac{1}{3}} \right\} \tag{20}$$

The last term is always positive and tends to infinity as $v_r \to 0$; it therefore gives a formal representation of the fact that the amount of any liquid which can be imbibed by a cross-linked polymer is finite.

Experimental determination of the free energy of dilution.—The theory outlined in the previous section leads to the conclusion that the driving force responsible for the imbibition of liquids by polymers is the large increase of entropy thereby produced; this increase has been estimated quantitatively. The controlling factor in determining the free energy of dilution in various systems is, on this view, the heat of dilution, and the form and approximate magnitude of this have also been estimated. There is at present a great lack of precise data by which these conclusions may be tested. Rough vapor-pressure data for a number of polymer–liquid systems give reasonably accurate values of ΔG_0 [by Equation (2)] but in very few cases is even the sign of the heat of dilution known with certainty. There is, however, abundant evidence that aqueous systems in general are not covered by the theory as developed, since for these ΔH_0 and ΔS_0 are both usually negative[16]. This discrepancy undoubtedly arises from the attachment of the water molecules to the polymer by hydrogen bonds, thus giving the swollen polymer a relatively high degree of order. It is clear that effects of this nature become increasingly probable as the system considered becomes more polar, and that the theory which has been developed can only be expected to hold for relatively nonpolar materials. In the following discussion, aqueous systems will, therefore, be ignored. It must also be pointed out that volume changes which accompany swelling have been implicitly neglected. Where these occur they make large contributions

to both the heat and the entropy of dilution, but always in the same direction, leaving the free energy approximately that to be expected if the volume had remained constant. Thus, *e.g.*, the swelling of natural rubber in *n*-pentane is accompanied by a considerable contraction and, in consequence, both ΔH_0 and ΔS_0 must be much lower than would otherwise have been the case[17].

By far the most complete data available are those for natural rubber and benzene, which cover practically the whole range of composition at different temperatures[18]. The free energy of dilution is therefore, known accurately from $v_r = 0.005$ to 0.999, and the heat and entropy of dilution approximately. The results are summarized in Figures 1 and 2; the former shows how accurately

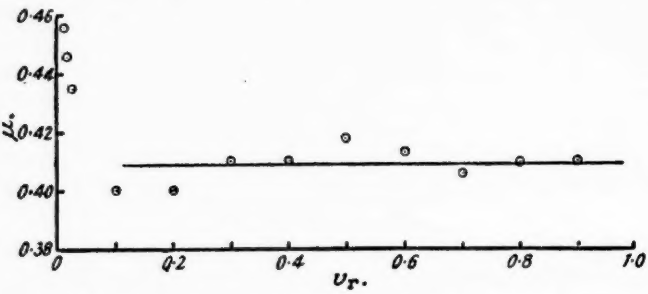

FIG. 1.—Free energy of dilution: natural rubber + benzene.

$$\mu = \frac{1}{v_r^2}\left\{\frac{\Delta G_0}{RT} - \ln(1 - v_r) - v_r\left(1 - \frac{1}{x}\right)\right\}.$$

FIG. 2.—Thermodynamic data for natural rubber and benzene.

Curve 1: $\Delta H_0/v_r^2$. Curve 3: $T\Delta S_0/v_r^2$, theoretical ($z = \infty$)
Curve 2: $T\Delta S_0/v_r^2$. Curve 4: $T\Delta S_0/v_r^2$, theoretical ($z = 4$).

Equations (17) and (18) describe the data, with a single value of μ. Despite this striking success, Figure 2 reveals that $\Delta H_0/v_r^2$ is far from being constant, while $T\Delta S_0/v_r^2$ shows corresponding deviations from the predicted form. The data for the heat of dilution cannot be represented by Equation (11), the dependence of $\Delta H_0/v_r^2$ on v_r being different in form from that to be expected from this equation. Furthermore, the heat of dilution of squalene, which contains six isoprene units, by benzene[19], is in good accord with Equation (10). These deviations are, therefore, believed to arise from the failure of the theory to allow correctly for intramolecular polymer–polymer contacts. This defect in the theory of dilute solutions has already been discussed; the experimental data suggest that the effect extends to quite high concentrations. It is found that the data can be understood by supposing that in an infinitely dilute solution of natural rubber in benzene some 23 per cent of the contacts made by sections of the rubber chain are intramolecular. The constancy of μ means that the low heat of dilution is balanced by a correspondingly low entropy of dilution, leaving ΔG_0 almost equal to the theoretical value.

Data for other polymer–liquid systems are for the most part confined to a single temperature, or of insufficient accuracy to justify the calculation of ΔS_0 from Equation (3). Huggins[5] has shown that the bulk of such data can be satisfactorily represented by Equations (17) and (18) with constant μ. The results for nonsolvents which are very poor swelling agents show small deviations. For instance, for natural rubber + acetone at 35° Lens's data[20] require a variation of μ from 1.5 at $v_r = 1$ to 1.3 at $v_r = 0.75$ (the limit of imbibition). Similarly[18] for natural rubber + methyl alcohol at 30° μ diminishes from 4.7 to 3.6 during the absorption of 2.5 per cent of alcohol, while $\Delta H_0/v_r^2$ falls by a factor of at least 10.

Perhaps the most striking success of the theory lies in giving so accurately the absolute magnitude of the entropy of dilution. Although Figure 2 reveals errors in the form of the ΔS_0–v_r curve, it shows that ΔS_0 has been calculated correctly within a factor of 2. When it is recalled that the theories current before the modern statistical treatment gave values of ΔS_0 too small by a factor of 1000, it is evident that a very great advance has been made.

These limited tests of the validity of the fundamental statistical results are sufficiently successful to warrant the use of the theory in discussing equilibrium properties of polymer solutions and gels; two examples are given in the next section.

(a) *Oil-resisting rubbers.* (b) *Solvents and plasticizers for polymers.*—The greater resistance of certain synthetic rubbers to hydrocarbons such as gasoline compared with natural rubber, has led to their being termed "oil-resisting." This description is a complete misnomer, since these rubbers differ from natural rubber only in being resistant to a different class of liquid. The general problem is to find a polymer which is relatively unaffected by a specified liquid or liquids. The problem of selecting a solvent or plasticizer for a given polymer is the exact converse, and the two can be discussed together. It will be assumed that a plasticizer is simply a liquid of low vapor pressure which is readily compatible with the polymer.

It has been shown that the behavior of a polymer–liquid system can be characterized by a single constant μ. Now the thermodynamic condition for a polymer to be resistant to a liquid is that ΔG_0 shall be zero at a fairly large value of v_r. Inspection of Equation (18) shows that this will be the case when μ is large; the controlling effect of μ is illustrated by Figures 3, in which $\Delta G_0/Tv^2$

is plotted against the degree of swelling $Q(= 1/v_r - 1)$ for various values of μ. If μ is small, the liquid is a solvent or a good swelling agent; as μ increases, the maximum swelling decreases rapidly. It is clear, therefore, that to be able to choose a plasticizer for a given polymer, or a polymer to be used in contact

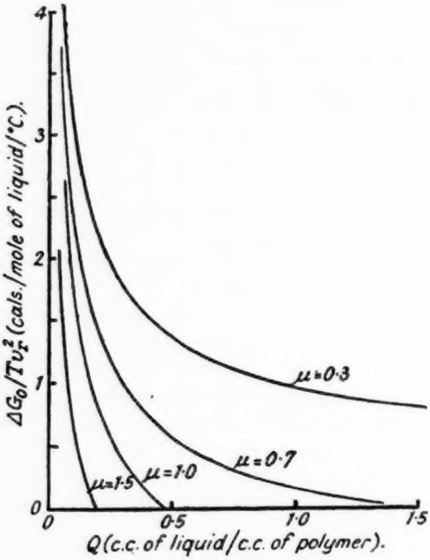

FIG. 3.

with a specified liquid, it is necessary to find what physical properties of the polymer and liquid determine the magnitude of μ. Equations (14) and (16) give the basis of the answer to this problem; combining them, we have:

$$\mu = \mu_0 + \frac{V_0}{RT}(\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \tag{21}$$

μ_0 is in general small (<0.5), so the magnitude of μ is determined essentially by the difference between the cohesive energy densities of the liquid and the polymer. Equation (21) is not found to be quantitatively valid; values of μ calculated by its aid are generally too small, but it has been used with considerable success in the following qualitative manner. Consider the swelling or solution of a given polymer in a range of liquids, arranged in order of increasing cohesive energy density. Equation (21) requires that μ should be large for the liquids of lowest E_{00}, should pass through a minimum for liquids having $E_{00} \sim E_{rr}$, and then increase again. Corresponding with these changes of μ, the liquids having greatest solvent or swelling power should be found at that point of the range where $E_{00} \sim E_{rr}$. In general, E_{rr} is not known, although it can be estimated approximately from the chemical nature of the polymer. A quantitative estimate may be made by using a cross-linked polymer, finding the liquid having the greatest swelling power, and then assuming its cohesive energy density to be equal to that of the polymer[21]. Given E_{rr}, a plot of the maximum swelling Q_m in this range of liquids against

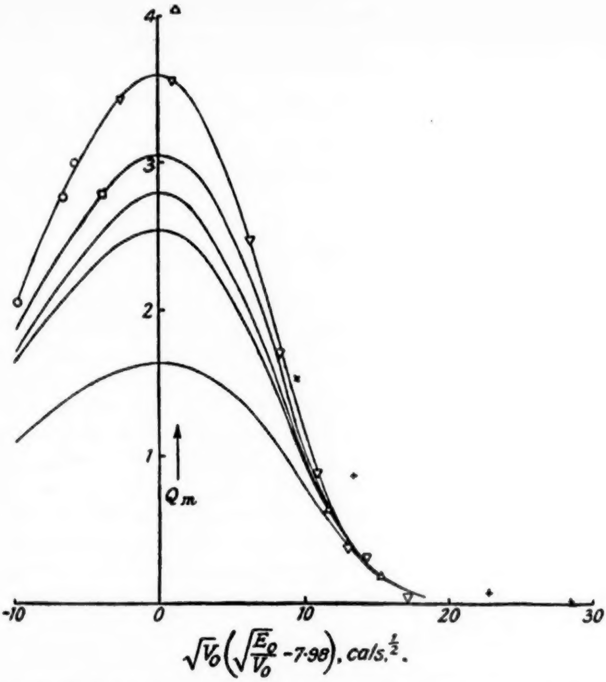

Fig. 4.—Swelling of five natural rubber vulcanizates in a range of aliphatic liquids.
Points (top curve only): ○ Hydrocarbons, □ Ethers, ▽ Esters, △ Ketones, × Aldehydes, + Nitriles.

$(\sqrt{v_0})(\sqrt{E_{00}} - \sqrt{E_{rr}})$ should, according to Equation (21), give a smooth curve, on which liquids of different chemical type should all fall. This in general is not quite true, but it holds surprisingly well for the swelling of natural-rubber vulcanizates in a wide range of aliphatic liquids[22], as is shown in Figure 4.

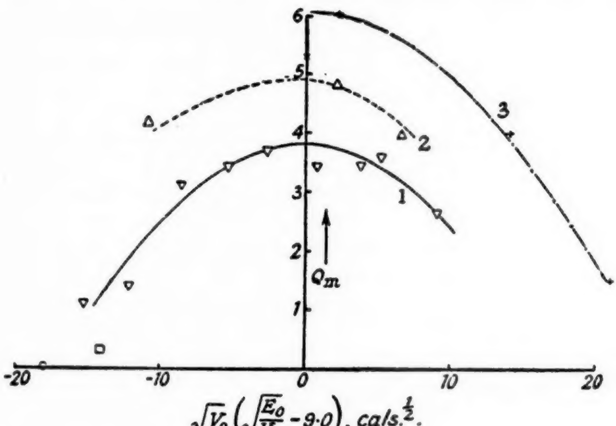

Fig. 5.—Swelling of a Thiokol-RD vulcanizate in a range of aliphatic liquids.
Curve 1: Esters. Curve 2: Ketones. Curve 3: Nitriles.

The five curves are for very different compounds, and it is clear that there is no essential difference between their swelling behavior. Aromatic liquids have in general a greater swelling power than aliphatic, for a given value of the abscissa[10]. With some of the more polar synthetic rubbers, different groups of aliphatic liquids do not fall on the same curve although, as illustrated in Figure 5, the positions of the maxima usually agree. To fit the data quantitatively it is, therefore, necessary to generalize Equation (21) empirically to the form:

$$\mu = \mu_0 + \beta \frac{V_0}{RT} (\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \tag{22}$$

where μ_0 and β may be somewhat dependent on the chemical natures of the liquid and the polymer. This limitation is not sufficient to diminish seriously the usefulness of this method of approach to the converse problems of selecting (1) polymers having solvent resistance and (2) solvents and plasticizers.

Conclusions.—In this brief survey, an attempt has been made to outline the statistical thermodynamic approach to the equilibrium properties of polymer solutions. It is clear that current theories, although crude, do give a surprisingly accurate quantitative account of the free energy of dilution. The separate calculations of the heat and entropy of dilution are less satisfactory, particularly in the region of dilute solutions, where a new statistical approach appears to be required. A more adequate statistical treatment of polymer-liquid systems, in which the heat of dilution is large or in which considerable volume changes occur, will almost certainly have to await advances in the understanding of the liquid state. Notwithstanding these limitations, the theory in its present form is capable of giving a semiquantitative answer to a number of practical problems. One of these has been discussed above; a similar order of agreement between theory and experiment can be obtained in the other problems listed in the introduction.

REFERENCES

1 Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942).
2 Gee, *Trans. Faraday Soc.* **40**, 463, 468 (1944).
3 Huggins, *J. Chem. Physics* **9**, 440 (1941); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Phys. Chem.* **46**, 1 (1942); *Ind. Eng. Chem.* **35**, 216 (1943); Flory, *J. Chem. Physics* **9**, 660 (1941); **10**, 51 (1942); Miller, *Proc. Cambridge Phil. Soc.* **38**, 109 (1942); **39**, 54, 131 (1943); Guggenheim, *Proc. Roy. Soc.* **183A**, 203, 213 (1944); *Trans. Faraday Soc.* **41**, 107 (1945); Orr, *Trans. Faraday Soc.* **40**, 306, 320 (1944).
4 Flory, *J. Chem. Physics* **9**, 660 (1941); **10**, 51 (1942).
5 Huggins, *J. Chem. Physics* **9**, 440 (1941); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Chem. Physics* **46**, 1 (1942); *Ind. Eng. Chem.* **35**, 216 (1943).
6 Miller, *Proc. Cambridge Phil. Soc.* **38**, 109 (1942); **39**, 54, 131 (1943).
7 Van Laar, *Z. physik. Chem.* **137A**, 421 (1928).
8 Hildebrand, "Solubility", New York, 1936.
9 Scatchard, *Chem. Reviews* **1**, 321 (1931).
10 Gee, *Trans. Faraday Soc.* **38**, 418 (1942).
11 Orr, *Trans. Faraday Soc.* **40**, 306, 320 (1944).
12 Guggenheim, *Proc. Roy. Soc.* **183A**, 203, 213 (1944); *Trans. Faraday Soc.* **41**, 107 (1945).
13 Orr, *Trans. Faraday Soc.*, in press.
14 Flory, *J. Chem. Physics* **13**, 453 (1945).
15 Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
16 Katz, *Ergebn. Exakt. Naturwiss.* **3**, 316 (1924); Urquhard and Williams, *J. Text. Inst.* **15**, 559 (1924); Fricke and Luke, *Z. Elektrochem.* **36**, 309 (1930).
17 Gee, unpublished work.
18 Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942); Gee and Orr, *Trans. Faraday Soc.* **42**, 507 (1946).
19 Ferry, Gee and Treloar, *Trans. Faraday Soc.* **41**, 340 (1945).
20 Lens, *Rev. trav. chim.* **51**, 971 (1932).
21 This process can be refined by using a graphical method of finding the maximum of the swelling E_{00} curve (see Gee, *Trans. Inst. Rubber Ind.* **18**, 266 (1943)).
22 Gee, *Trans. Inst. Rubber Ind.* **18**, 266 (1943).

PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. IV. CORRELATION BETWEEN STRUCTURE AND PROPERTIES OF ELASTOMERS DERIVED FROM DIENES *

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INTRODUCTION

The preparation of polymers from dienes has been discussed in Parts I and III of this investigation[1]. It is the purpose of the present paper to discuss the physical, mechanical, and chemical properties of the polymers in relation to their structures. Evidence from very different branches of science must be compiled for an evaluation of essential structural factors; the use of natural rubber (abbreviated NR) and gutta-percha as an ultimate standard of regularity makes a relative comparison possible. This "ideal" regularity of NR can be modified in a number of ways. Addition of hydrogen chloride to the double bond and subsequent removal of the same compound leads to isorubber, which still retains much of the regular chain, but lacks the preponderance of *cis* or *trans* groups, as well as the regular sequence of the double bonds. Addition of hydrogen chloride as such leads to a paraffinic polymer with a polar group, while partial halogenation under special circumstances leads to an olefinic polymer with the same polar group. Detailed results of such studies on derivatives of NR will be given in further papers, but evidence relevant for the determination of polymeric structure is included in this discussion.

In the course of an investigation on the diffusion of gases through elastomers, it has been found by van Amerongen[2] that the heat of activation for the diffusion process increases with the number of methyl groups in the molecular unit. The influence of —CH_2—CHR— groups derived from 1,2- or 3,4-addition during formation of the polymer chain must be taken into account simultaneously with that of the methyl groups. The properties of copolymers, which will be discussed in more detail later[3], enable us to draw some additional conclusions on the role played by 1,2-addition. Additional information on the mobility of molecular groups can be obtained from studies on second-order transition phenomena. Boyer and Spencer[4] have correlated the second-order transition point with molecular properties, while Liska[5] and Borders and Juve[6] have produced ample proof for the fundamental significance of the brittle point as a molecular property. Methyl groups and 1,2-addition are of importance for the mobility of the "flow units" in the polymer chain, but they are also interlinked with the formation of the polymer. Methyl groups exert a directing influence on the rate of 1,2-addition, competing with 1,4-addition during polymerization. This combined evidence can be linked to the elastic properties of the polymers.

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A number of structural features have an equally important effect on the formation of the polymers as well as on their properties, and it is therefore impossible to deduce a quantitative correlation between those properties and one particular change in structure. There are, however, groups of experimental results in which one or two of these structural factors become predominant.

Correlations between synthesis and structure will be treated in Section I, followed by a discussion of mechanical properties in Sections II and III, while the influence of structural symmetry in connection with the complex compounds of silver nitrate and with halides will be dealt with in Sections IV and V. The hydrochlorides from NR are the link between the field of olefinic elastomers and that of paraffinic elastomers and plastics; their position within the latter group will, therefore, be discussed last.

I. CORRELATIONS BETWEEN REACTIVITY OF DIENES AND STRUCTURE OF POLYMERS

We shall first discuss the reactivity of butadiene and the properties of the resulting polymers, and then consider the directing influence of methyl groups.

1,2- AND 1,4-ADDITIONS

It has been found empirically that the amount of 1,2-addition in radical-initiated butadiene polymers and copolymers does not exceed 20–25 per cent[7]. In alkali metal-catalyzed polymerization, 1,4-addition is known to possess an overall activation energy about 5 kcal. higher than that of 1,2-addition[8]. The absolute value of this quantity is also influenced by the nature of the metal[9]. Russian and German Buna, produced at low temperatures, therefore contains about 40 per cent of vinyl groups from 1,2-addition[10].

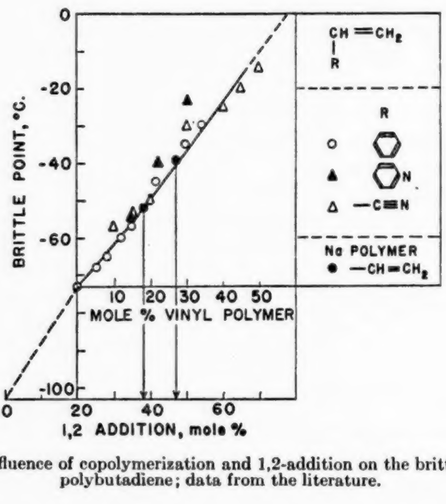


FIG. 1.—Influence of copolymerization and 1,2-addition on the brittle point of polybutadiene; data from the literature.

The main effect of 1,2-addition on the physical properties of the polymer should be similar to that of the incorporation of a vinyl copolymer. Figure 1 demonstrates this point. The brittle points of emulsion copolymers[5] are an almost linear function of the vinyl compounds. Only small individual differ-

ences between comparable substituents become apparent. The brittle points of sodium-polymerized butadiene[6] correspond to those of copolymers with 20–30 per cent of vinyl compounds. Since the emulsion polymer from butadiene already contains 20 per cent of 1,2-groups, the linear correlation suggests a value of 40–50 per cent of vinyl groups in Buna, which is in good agreement with data from ozonolysis[10]. It follows from Figure 1 that the (hypothetical) straight-chain 1,4-polybutadiene should have a brittle point below $-100°$. As will be discussed later[5], the correlation shown in Figure 1 also exists between the copolymers derived from isoprene and dimethylbutadiene.

CONSECUTIVE REACTIONS

These empirical results indicate prevalent formation of 1,4-groups with radicals which may be connected with favorable resonance energy of the growing 1,4-radicals. The nature of the consecutive reactions, caused by the vinyl side groups in the polymer, which determine the ultimate structure of the polymer is readily understood.

Sodium does not react with the double bond of such vinyl groups in, *e.g.*, Buna-115. This polymer therefore consists essentially of a substituted straight-chain polymer; this chain is comparable with that of polystyrene or Butyl. The plastic elastic properties are determined by the comparatively high brittle point, and the polymer softens readily at higher temperatures. The original extensibility, softness, and plasticity of these polymers can be altered by reactions with compounds attacking the isolated or vinyl double donds[11].

In radical-initiated polymerization the situation is quite different. Here vinyl side groups compete with the diene as acceptors for free radicals and the polymer, isolated at high yields[12] therefore has the now generally assumed brush structure. These polymers consist of shorter straight chains, which are irregularly interlinked by reactions of the vinyl groups; since these short-chain fractions are less interrupted by 1,2-addition than are sodium polymers, they have a lower brittle point.

INFLUENCE OF METHYL GROUPS

By applying the same line of thought to the polymers derived from a methylated butadiene, we can draw the following conclusions about 1,2-addition and the consecutive reactions.

As has been pointed out[12], the enhanced reactivity of allylic hydrogen in the methyl groups attached to a vinyl side group reduces the probability of a reaction between the double bond and free radicals[13]. The plasticity, as well as the solubility, of polyisoprene, Methyl rubber, and the polymers from methylpentadiene, is much greater than that of the corresponding polybutadiene prepared by radical-initiated reactions. This strongly indicates a decrease in cross-linking, due to a reduced number of consecutive reactions. In addition, there is also the following indirect evidence that the vinyl groups in these polymers are not only less reactive, but also present in smaller quantities.

(1) We have already shown[14] that the tendency to dimerize at 100° decreases with the relative ratio (diene:relative rate of dimerization) as follows: butadiene:isoprene:2,3-dimethylbutadiene = 1:0.57:0.29. Starting from the empirical result of 20 per cent of 1,2-addition for polybutadiene, and assuming a correlation between the acceptor properties in the Diels-Adler reaction and the tendency to undergo 1,2-addition, the above figures suggest 12 per cent of

1,2- or 3,4-addition for polyisoprene and only 9 per cent of 1,2-addition for Methyl rubber.

(2) By using a special method of pyrolysis, Boonstra and van Amerongen[15] were able to depolymerize NR with a yield of 58 per cent isoprene, a figure which is in good agreement with that obtained from the pyrolysis of dipentene[16]. With the same method, van Amerongen[17] obtained the following yields of dienes from the polymers:

Polymer	Buna-115	Buna-S	Polyisoprene	Methyl rubber
Diene (percentage)	8	14	46	58

These data indicate regularity of the chain structure in Methyl rubber, approaching that of NR, and a decrease of regularity in the expected order. Sodium-polymerized isoprene is obviously different from the product obtained by radical initiation, as both the brittle point[6] and the infrared spectrum[18] indicate a high fraction of vinyl side groups.

CYCLIZATION AND ISOMERIZATION

The well-known tendency of natural rubber to cyclize, *i.e.*, to undergo partial transformation of an aliphatic terpene into a cyclic one[19], is also common to polyisoprene and methyl rubber[20]. Such cyclo groups reduce the mobility of the straight-chain molecule and therefore increase the brittle point of the polymer, as can be seen from the mechanical properties of cyclorubber. Even small quantities exert a considerable effect, as the loss of every double bond leads to an immobilization of at least two molecular units.

Isorubber[21] prepared by removal of hydrogen chloride from rubber hydrochloride retains nearly all of the original number of double bonds, but loses the ability to crystallize, and therefore the superior mechanical qualities, of NR. This illustrates the importance of a preponderant *cis* structure, aside from a straight-chain structure.

II. INFLUENCE OF METHYL GROUPS AND CHAIN STRUCTURE ON PHYSICAL AND MECHANICAL PROPERTIES OF POLYMERS

ELASTIC PROPERTIES

We have shown in the foregoing section that the regularity of a chain depends on the course of the polymerization reaction, which in turn is influenced by the structure of the diene. We shall now consider further experimental evidence on the correlation between structure and physical properties (see Table I).

Methyl groups in the molecular unit increase intermolecular attraction and may lead, therefore, to higher densities. Crystallization (gutta-percha) and cyclization (isorubber), however, interfere with this phenomenon. One chlorine group exerts a much more pronounced effect on density than one methyl group; in the case of Neoprene, partial crystallization prohibits a more quantitative comparison.

Consideration of kinetic tests offers more convincing evidence of the influence of methyl groups. It follows from Table I that brittle points and elastic recovery change in the same direction, although the type of mechanical deformation is very different for the two methods.

Brittle points, as well as the closely related second-order transition points, are gradually raised by the introduction of methyl groups into the molecular

Table I

Influence of Polymer Structure on Some Physical and Mechanical Properties

Polymer	Substituents on butadiene unit	Density (20° C)	Second-order transition point† (° C)[4]	Brittle point† (° C)[23]	Rebound elasticity (min.) (temp.† ° C)[24]	Per cent set at 0° after 5-minutes' recovery from 100% extension	Activation energy of gas diffusion (kcal.)[25] Hydrogen	Nitrogen
1,4-Polybutadiene				(< −100)	(≪ −60)			
Emulsion polybutadiene		0.907	(−85)	−80	(< −60)	5–10	5.1	7.2
Buna-115				−40	−30	5–10		
Natural rubber		0.910	−73	−58 to −53	−60	2–5	5.9	8.7
Polyisoprene		0.919		−57		15–20		
Isorubber	CH_3	0.940				5–10		
Gutta-percha		0.96*		−54	(> +50)*	100*	7.6*	9.8*
Neoprene-G	Cl	1.244*		−40	−20	80–100*	6.6	10.3
Methyl rubber	CH_2	0.941	(−60 to −50)	−30	+20	50–30	7.5	12.4
Polymethylpentadiene[22]	CH_2			−1	(> +20)			

* Value influenced by amount of crystalline fraction.
† Figures in parentheses are estimates.

unit. The effect of one chlorine atom is again larger than that of one methyl group, but smaller than the increase in brittle temperature caused by two methyl groups.

The limiting temperature for elastic recovery is related to the minimum temperature of rebound elasticity. The available data indicate the simultaneous influence of methyl groups, partial crystallization[5], and regularity of the chain. There is, however, no doubt that at least the introduction of a second methyl group has a pronounced influence on the rebound elasticity. Similar conclusions can be drawn from the rate of elastic recovery at 0°. This difference between polyisoprene and Methyl rubber is even more emphasized by the rate of recovery at different temperatures (see Figure 2).

The factor which the brittle point and the elastic recovery have in common is an activation energy necessary for the rotation of molecular units. The magnitude of this factor is closely related to the energy of activation calculated from the permeation of gases. In fact, the data (Table I) for both hydrogen

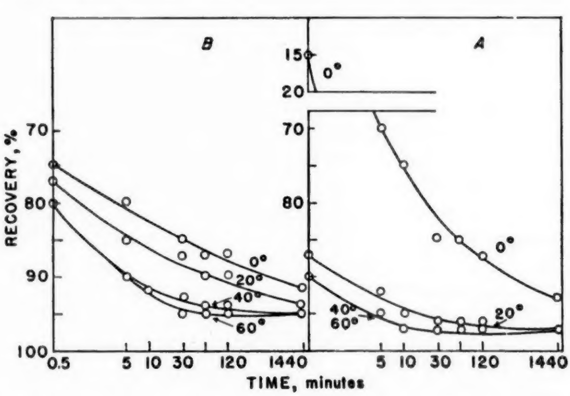


Fig. 2.—Rate of elastic recovery at various temperatures after an original extension of 100% pure-gum vulcanizates: (*A*) Methyl rubber; (*B*) polyisoprene.

and nitrogen show not only the same increase in the series: polybutadiene, NR, Methyl rubber, but indicate again the stronger influence of the second methyl group. Here also the values for Neoprene fall between those of NR and Methyl rubber. The rates of diffusion from which these quantities are derived do not necessarily show the same regularity, as changes in the energy of activation are partly counterbalanced by the temperature-independent factor.

The postulated low brittle point of the hypothetical 1,4-polybutadiene is in good agreement with the findings of Kistiakowsky and co-workers[26] It is well known from these thermochemical studies that the rotation of a methylene group is eased by the neighboring double bond. Any interruption of the regular sequence (double bond, single bond) in polybutadiene leads to stiffening of the chain. This explains the influence of copolymerization and 1,2-addition, as illustrated by Figure 1, but the reduction of molecular mobility caused by methyl groups requires another explanation: intermolecular attraction is increased by substituting the —CH— groups by $—C(CH_3)—$ groups in the flow units.

STRESS-STRAIN PROPERTIES

We shall now turn to the discussion of moduli at room temperature, keeping in mind the fact that polymer structure also influences the temperature dependence of this quantity. We can derive the following series of decreasing extensibility from Figure 3:

NR > Butyl > Methyl rubber > polyisoprene > isorubber > sodium-Buna > emulsion polybutadiene

The differences between the first three members of the series are probably determined by the tendency to crystallize, which is somewhat counterbalanced by a decrease in molecular mobility at room temperature, as indicated by increasing brittle points. The significant quantity in this comparison is the change of modulus at a certain elongation, and not the tensile strength at break. The modulus of Methyl rubber varies at 600 per cent elongation by a factor of 10, depending on the degree of polymerization and vulcanization. The slopes of the curves are comparable to those of Butyl rubber, which vary as a function of molecular weight and unsaturation. Such variations are similar to those found for NR as a function of the degree of vulcanization. Figure 3 suggests strongly that the essential differences between Methyl rubber and the other two polymers is the lack of ability of the former to crystallize on stretching.

The other members of the series show a simultaneous decrease in extensibility and brittle points. Since the latter means an increase in molecular mobility at the same temperature, correlation with structural properties becomes more difficult. Only the extraordinarily high modulus of 25 kilograms at 100 per cent extension found for emulsion polybutadiene suggests the preponderance of a different mechanism of elasticity[27], which becomes prevalent even at moderate extensions for a chain of irregular structure.

The addition of carbon black produces similar intermolecular forces in all polymers. The differences in moduli become more a function of cross-linking by vulcanization than of the original polymer structure. The extensibility, however, is still correlated to the structure, as can be seen from Figure 4.

In the series of Methyl rubbers, the low-yield, very soft polymer I is distinctly less extensible than the high-yield polymers II and III. The quality of polymethylpentadiene falls between those limits. Buna-115 also falls

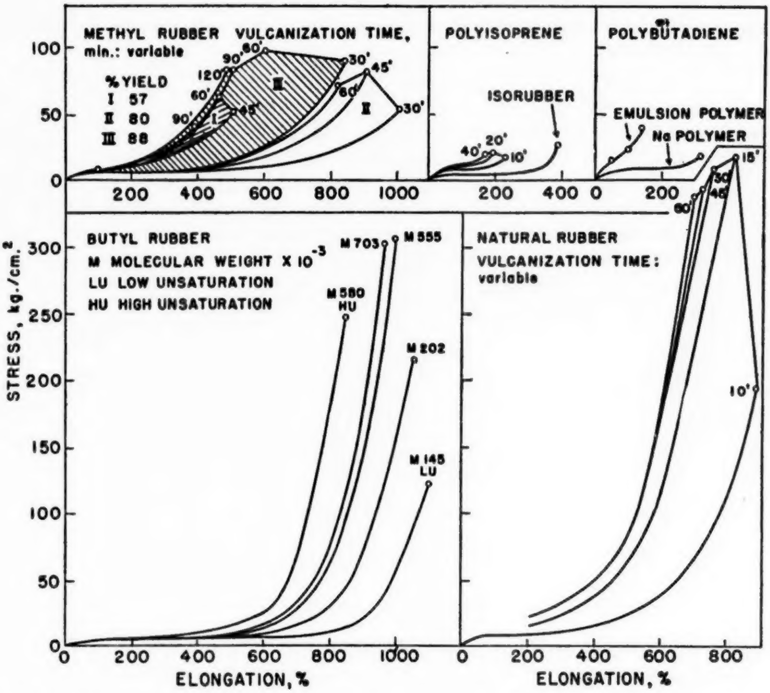


FIG. 3.—Tensile properties at room temperature of pure-gum vulcanizates from polydienes and natural rubber prepared with ultra-accelerator at 110° C, and Butyl after Flory[28].

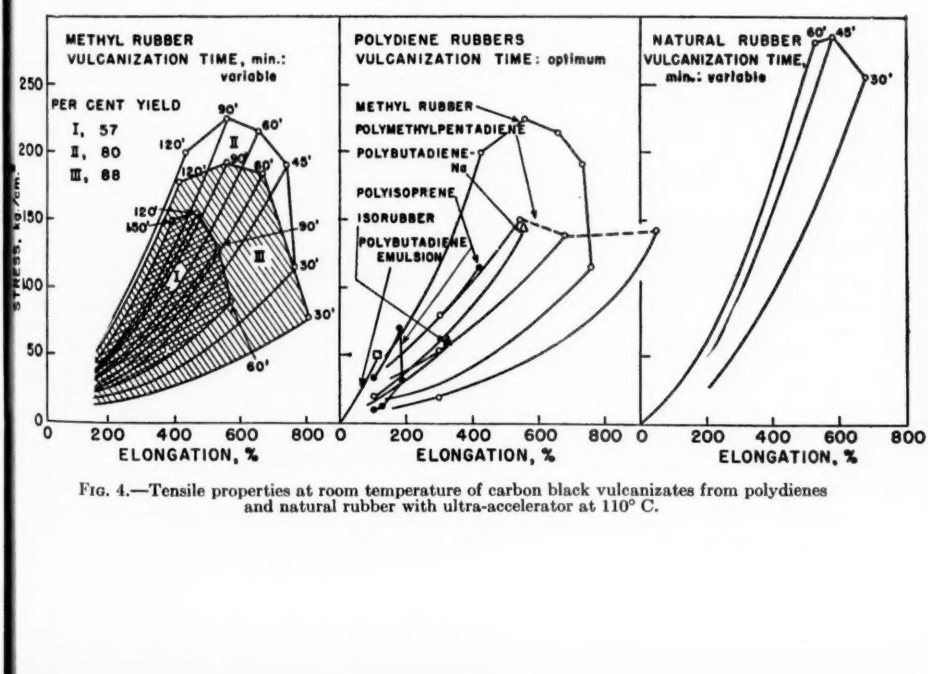


FIG. 4.—Tensile properties at room temperature of carbon black vulcanizates from polydienes and natural rubber with ultra-accelerator at 110° C.

within this limit, while isorubber does not differ essentially from polyisoprene. The extensibility in the series of polydienes decreases in the same order as has been established for the pure gum vulcanizates.

The set of experiments summarized in Table I gives us some information on the influence exerted by the molecular units, and Figures 3 and 4 indicate the importance of a straight-chain structure. If we now try to place Neoprene in these series, it clearly occupies a position between those of Butyl and NR. This, however, is a fortuitous result, due mainly to the higher tendency to crystallization which is common to halides in general. A comparison of the diverging tensile properties of elastomers at higher temperatures, which will be given in the following section, reveals the incidental similarity between NR and Neoprene at room temperature.

EXPERIMENTAL DATA

The preparation of polymers has already been discussed[1]. Isorubber has been prepared from the hydrochloride with slightly alkaline, aqueous solutions and an organic solvent. Isorubber is cyclized to about 10 ± 5 per cent, partly oxidized, and very susceptible to further oxidation.

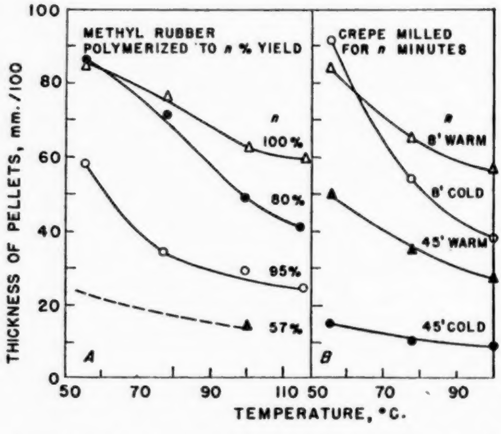


FIG. 5.—Hardness of Methyl rubber and natural rubber as a function of temperature.

Properties of raw polymers.—Only polybutadiene prepared by radical catalysis was too hard for a comparison of plasticity with NR on the instrument used. The plasticity of all other polymers falls within the limits of warm and cold plasticized NR, the absolute value depending on conditions of polymerization.

A relative comparison was made on the steam plastometer[29]. The thickness of pellets was measured after 15 seconds of compression. This method offers the advantage of experimenting with small quantities, but a theoretical interpretation of the resulting figures is difficult[30]. Figure 5 may serve as an example, showing the influence of synthesis on the plasticity of Methyl rubber. The density of raw and vulcanized polymers was determined by the hydrostatic method. In addition to the figures reproduced in Table I, results are summarized in Table II.

TABLE II
SPECIFIC GRAVITY OF POLYMERS

Temperature (° C)	Polybutadiene	Polyisoprene	Methyl rubber
	Raw polymer, $d_4^{t^0}$		
+1	0.918	0.937	0.952
20	0.907	0.919	0.938
50	0.889	0.902	0.923
Coefficient of expansion × 10^4	6	6	6
	Pure gum vulcanizates, $d_4^{t^0}$		
+1	0.976	0.991	1.00
20	0.963	0.980	0.991
50	0.940	0.958	0.976
Coefficient of expansion × 10^4	7–8	7–8	6

The temperature coefficient of thermal expansion is in agreement with the value found for other elastomers (see Part V). The brittle points of Methyl rubber (Table I) and some derivatives of natural rubber (Table VII) were determined only by hand tests, but with an accuracy of ±2°.

Mixing was done on a Thropp mill, which permitted the investigation of very small quantities. The breakdown of NR on this mill was distinctly slower than on an ordinary mill; otherwise conditions were identical with those of usual laboratory procedures.

Vulcanization was carried out either in an electrical press or in a steam autoclave. The maintenance of pressure during cooling (to avoid the formation of gas bubbles) is essential for the preparation of samples from nonconventional polymers. Plates 1 mm. in thickness were used throughout the study.

Formulas were kept as simple as possible (see Table III), but had to be adjusted to the type of polymer. Since Methyl rubber is difficult to handle at 142°, an ultra-accelerator was generally used with this elastomer. Polybutadiene, on the other hand, should be vulcanized at 142° as it does not flow sufficiently around 100°. Polyisoprene can be vulcanized under both conditions.

Tensile strength and elongation at break were measured on a Schopper dynamometer. Dumbbells (dimensions = 3.2 × 1 × 1 mm.) were used throughout the investigation. Elongation at break is expressed in percentage of the original length. Strength in kg. per sq. cm. is referred to the original cross-section unless otherwise stated. Rate of recovery was measured after an elongation to 100 or 200 per cent for 24 hours. The permanent set was measured after release between 0.5 minute and 24 hours. Measurements at 0° were

TABLE III
VULCANIZATION FORMULAS

Component	Parts by weight			
Elastomer	100	100	100	100
Zinc oxide	5	5	5	5
Vulcazit-AZ	1.8		1.8	
Vulcazit-P Extra N		1.5		1.5
Stearic acid	2	2	2	2
Carbon black			44	44
Phenyl-β-naphthylamine	2	2	2	2
Sulfur	1.5	2	1.8	3
Temperature of vulcanization (° C)	142	110	142	110

done the same way as at ordinary temperatures, but those at higher temperatures had to be modified by stretching the polymer at room temperature for 24 hours and then adjusting the extended sample to higher temperatures.

Since Methyl rubber can be conveniently prepared, extensive experiments were carried out to evaluate the influence of synthesis. In addition to Figures 2, 3, and 4, Tables IV and V provide further information and a comparison

TABLE IV

INFLUENCE OF POLYMERIZATION ON PROPERTIES OF METHYL RUBBER

	Preparation				Properties	
No.	Catalyst	Temp. (° C)	Time (hours)	Yield (%)	Solubility in benzene at 20°	Hardness (mm. × 10^{-2})
1		100	2136	57	Soluble	14
2	1% DAB	70	2232	80	2.7%	48
3	1% DAB	100	96	88	Insoluble	23
4	1% DAB	100	168	95	Insoluble	29
5	1% DAB	100	504	100	Insoluble	62
6	Emulsion	50	20	95	Partly soluble	16
7	Sample from I.-G. Farben				Insoluble	88
	NR plasticized (45 min.) warm				Soluble	33

TABLE V

MECHANICAL PROPERTIES OF VULCANIZED METHYL RUBBER

No.	Vulcanization (min.)	T*B* (kg./sq. cm.)	EB (%)	Modulus (500%, kg./sq. cm.)	Per cent set after 1 hr. 20°	0°	Hardness (Shore A)
			Pure-gum mixtures (vulcanization temp. 110°)				
1	60	62	470			15	
2	45	81	910	11	25	50	
3	45	96	603	54		22	45
4	90	77	587	43		20	40
5	90	73	543	52		50	45
6	45	25	445			20	
Whitby	40	28	509	26			
NR	15	366	820	58	5	5	40
			Carbon black mixtures (vulcanization temp. 110°)				
1	120	155	468		17	75	
2	90	225	560	191	15	110	
3	90	192	560	161	10	75	70
4	60	173	600	117	10	35	75
5	90	185	585	185	7	125	70
6	90	137	562				
7	60	160	726				
Whitby	60	166	531	150			
NR	45	285	588	288	10	7	60

with the now classical experiments of Whitby and Katz[31]. Our values are generally higher than those found by Whitby and Katz. This is probably caused by the fact that the latter were not in the possession of an active catalyst and could therefore produce only low-yield polymers with inferior tensile strengths (as can be seen from Figures 2 and 3). Methyl rubber vulcanizes more slowly than NR; this is probably due to the accelerating influence of basic impurities in NR.

III. INFLUENCE OF HEAT AND SWELLING AGENTS ON TENSILE STRENGTH

The properties of pure-gum vulcanizates at 20° and high elongations are determined largely by the occurrence of crystallization, but mechanical properties at higher temperatures become different. It is essential to compare the tensile strength at the actual cross-section as both tensile strength and modulus change. Results are given for pure-gum and carbon black vulcanizates in Figure 6.

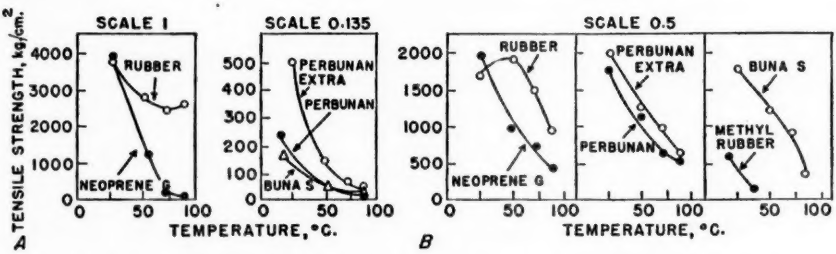


FIG. 6.—Influence of temperature on the tensile strength at break: (A) pure-gum vulcanizates, scales 1 and 0.135; (B) carbon black vulcanizates, scale 0.5.

It is obvious from Figure 6*A* that only NR retains its high tensile strength, whereas Neoprene at higher temperatures behaves like one of the noncrystallizing elastomers. Before the significance of this comparison is discussed, some further experimental evidence should be taken into account. Gutta-percha shares the straight-chain structure with NR. While the amount of crystalline phase in raw gutta is about 45 per cent[32], it is lower in an unstretched thiuram vulcanizate[33]. The influence of temperature on the tensile strength is illustrated by Figure 7. Above the melting point of the crystalline phase,

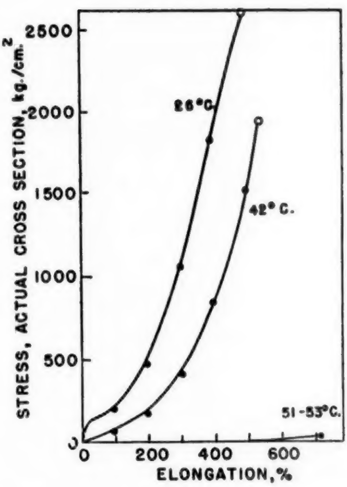


FIG. 7.—Influence of temperature on the stress-strain curve of vulcanized gutta-percha and thiuram mixture.

gutta-percha obviously behaves like Neoprene and not like NR. This result depends, however, on experimental conditions, as can be seen from the following experiment:

A strip of vulcanized gutta-percha was stretched 200 per cent and then heated to 70° C. Contrary to the expectation (based on Figure 7), it did not break after several hours; however, at 90° C it became mechanically weak, whereas NR can withstand this temperature.

A certain parallel also exists between the action of swelling agents and that of temperature on the tensile strength of elastomers[34]. The strength of Neoprene and other synthetics deteriorates faster than that of NR in the presence of solvents. We have shown in another paper that NR cannot be stretched more than 150 per cent in the swollen state, while even a weak swelling agent reduces the mechanical strength[35]. The latter effect is illustrated by Table VI.

TABLE VI

INFLUENCE OF WEAK SWELLING AGENT ON EXTENSIBILITY OF ELASTOMERS (PURE-GUM VULCANIZATES) AT VARIOUS TEMPERATURES WITH ISOAMYL ALCOHOL AS SOLVENT

	E_{rs} = EB in liquid: EB in air				
t (° C)	NR	Neoprene-G	Perbunan-Extra	Perbunan	Buna-S
20	1.00	0.70	0.65	0.55	0.45
50	0.80	0.60	0.60	0.40	0.30
70	0.85	0.50	0.45	0.30	0.20

The extensibility of all synthetics is reduced to a much greater extent by a weak swelling agent than that of NR, and this difference in mechanical properties becomes even more pronounced at higher temperatures. It should be mentioned that in the weakly swollen state, as well as at higher temperatures, the optimum value for NR is more sensitive to the degree of vulcanization[36] than under ordinary conditions. In other words the plateau occurring as a function of vulcanization time and sulfur concentration becomes smaller.

A tentative explanation for these diverging mechanical changes which occur under the influence of temperature and solvents will now be given. The low melting point of NR is caused by the ease of free rotation of methylene and methyl groups attached to a double bond[37]. This free rotation is reduced by the orientation of chains under strain. The melting point and solubility of the crystals therefore approaches those of normal paraffins. This degree of orientation of the chains is also dependent on the amount of cross-linking, which explains the more pronounced influence of the degree of vulcanization on the mechanical properties at higher temperatures.

High-sulfur vulcanizates of NR retain their mechanical strength even far above 100°[38]. Here the interaction of polar sulfur groups is favored by the orientation of the straight chains (see also the discussion of the properties of hydrochlorides, Section V). In addition, the formation and size of crystals also depend on the ratio of the rate of crystallization to the rate of orientation under extension. Differences in these rates may explain the unexpected results obtained with gutta-percha.

With Neoprene the situation is very different. The tendency to crystallize is caused by the much larger intermolecular forces, but the ease of rotation at higher temperatures—which tends to destory the crystal structure—is not counterbalanced by a straight chain, which in the case of NR preserves the crystalline configuration. As a consequence, the crystalline fractions in Neoprene are more easily broken down by heat than those of NR.

The reinforcing effect of carbon black is probably caused by resonance between loose electrons in the filler and (1) double bonds, (2) polar groups, and (3) aromatic groups in the polymer. Such interaction is likely to be smaller for units of type (1) than for types (2) and (3). This would explain why Methyl rubber, although it has a high brittle point, weakens much faster with increasing temperature than Buna-S, which has a low brittle point. In addition our hypothesis accounts for the fact that Neoprene and Perbunan become quite comparable to NR in carbon black mixtures, even at elevated temperatures (See Figure 6*B*). The resonance energy is likely to be much larger for the former than for NR, whereas the crystallization of NR is hampered by the presence of fillers.

Much additional experimental evidence is necessary to prove the correctness of the assumed resonance effect. It is, however, satisfying that the results, which are discussed in the following section, fit well into our picture.

EXPERIMENTAL

Measurements at elevated temperatures were carried out by mounting a mantle on the Schopper dynamometer and blowing warm air through it. Thermal equilibrium with the small test piece was reached after a short time.

The influence of organic liquids on tensile strength was tested by immersing a stretched strip of rubber in the liquid and interpolating the elongation at which the sample just failed to break in the swollen state.

IV. PROPERTIES OF COMPLEX COMPOUNDS WITH SILVER NITRATE

The formation of a complex compound from NR and silver nitrate was discovered in the laboratory of Mark[39], but only a comparison of this isolated observation with the molecular analogon, studied previously by Winstein and Lucas[40], leads to an understanding of the general nature of such equilibria.

Reversible Reaction

Winstein and Lucas found no isomerizing influence of silver nitrate on the double bond in *cis*- or *trans*-butene. We found the same to be true for the complex compound with NR. After the complex was dissolved in pyridine and the rubber was precipitated, no difference either in the unsaturation of the raw rubber or in the mechanical properties of the vulcanized samples was observed.

Amorphous Complex Compounds

The position of the equilibrium between:

$$AgNO_3 + \text{olefin} \rightleftharpoons [AgNO_3 \cdot \text{olefin}]$$

depends on the structure of the double bond and the olefin; most olefins are able to produce a complex compound in the liquid phase. It could, therefore, be expected that all olefinic polymers exhibit a tendency to form a complex with silver nitrate. This proved to be the case, but the properties of these complex compounds differ very much from those derived from NR and gutta. They are amorphous and therefore swell strongly in liquids like dioxane. In the swollen state they become very soft, and it is extremely difficult to remove the solvent completely.

Crystalline Complex Compounds

Crystallization occurs simultaneously with complex formation from swollen NR, and the dried crystallized complex compound swells only weakly in hexane, whereas a freshly prepared mechanical mixture of NR and silver nitrate is readily dissolved by hexane.

Winstein and Lucas isolated a solid complex compound from dicyclopentadiene (DCP) and silver nitrate and another from DCP and silver perchlorate. An *x*-ray investigation revealed both compounds to be crystalline, but with low symmetry[33]. These crystals show many analogies with those from NR and silver nitrate. They melt above 100°, whereas DCP and NR melt near 30°. They dissolve easily in strong solvents for the olefin and crystallize from weak solvents for the olefin. The high melting points indicate intermolecular forces, similar to those in silver nitrate and aromatic complex compounds. This analogy, however, is not complete. The complex compound from DCP occurs in the molecular ratio (1:1), while those from NR and gutta can be produced even with very small concentrations of silver nitrate. Moreover, the *x*-ray diagram of the rubber–silver nitrate complex changes with the concentration of silver nitrate in the complex[41]; this result is now under consideration.

Since neither polyisoprene[43] nor related compounds[36] show any tendency to crystallize with silver nitrate, the formation of the crystalline complex compound can clearly be taken as a measure of molecular symmetry.

Reinforcement

The mechanical mixture of polyisoprene and silver nitrate is soft like a mixture with an inert filler, whereas the complex compound is tough and becomes hard but still pliable with 30–40 per cent silver nitrate. This reinforcing action of silver nitrate is much more pronounced than that of carbon black, and is very different from the reinforcement caused by crystallization of NR. Winstein and Lucas were the first to interpret the existence of complex compounds, which are rapidly and reversibly formed, on the basis of Pauling's concept of resonance energy and the preliminary note by Baker and Pape[42] gives further support to the correctness of their assumption. It seems therefore justified to deduce from the experience that both silver nitrate and carbon black cause mechanical reinforcement of a noncrystallizing elastomer, the assumption that this effect is caused by the same type of molecular interaction, *i.e.*, intermolecular bonding by release of resonance energy.

EXPERIMENTAL

Kratky, Philipp, Posnansky, and Schossberger[39] produced the complex compound from NR by immersing a film from latex in a salt solution; this method is tedious, and an equilibrium is reached only slowly and incompletely. We have, therefore, substituted the following method. Powdered silver nitrate is milled into NR on a laboratory rubber mill (using rubber gloves). Samples of the soft rubber, containing silver nitrate as a filler, were immersed in a solution of silver nitrate, dioxane, and water. Hardening, caused by crystallization, occurs very soon, while an equilibrium value is approached after less than one day. The position of the equilibrium depends on the following factors: solvent, concentration of silver nitrate, and temperature. Crystallization, indicated by *x*-ray measurements, can also be produced without the use of a swelling agent.

Mixtures of synthetics with silver nitrate remain soft in the swelling agent and finally tend to dissolve in dioxane–water. The fact that polyisoprene does not dissolve in dioxane–water proves the formation of a soluble complex compound which becomes hard and pliable.

Complex compounds can be separated to their components by being dissolved in pyridine and precipitating the essentially unchanged polymer with alcohol–water. DCP–silver nitrate begins to decompose at 152° and melts at 156–158°. DCP–silver perchlorate explodes at +134°.

V. MECHANICAL PROPERTIES OF RUBBER HALIDES

There are two methods available for the introduction of polar chlorine atoms into the rubber chain: substitution of a hydrogen atom or addition of hydrogen chloride to the double bond. The significant difference in mechanical properties of olefinic and paraffinic monohalides will now be discussed.

OLEFINIC AND PARAFFINIC HALIDES

We have found that chlorine reacts with natural rubber in solution primarily by substitution, a result which is in good agreement with the findings of other authors[43]. Such partially chlorinated rubber is, however, very inhomogeneous. The chlorine contents of the fractions vary between 2 and 40 per cent. Using sulfuryl chloride as a source of chlorine, the situation becomes different. In the presence of peroxides and with carefully purified rubber or gutta-percha the chlorine from sulfuryl chloride adds to the double bond—in analogy with the behavior of olefins[43]. Using solutions made from ordinary NR sheet, the basic impurities induce a substitutive reaction to the extent of more than 80 per cent. These reaction products are very homogeneous on fractionation[44] and it is, therefore, possible to correlate the change in mechanical properties to that of structure. Using a new method of kinetic analysis (unpublished results), the allylic nature of the chlorine has been established and, by a comparison with molecular models, it was possible to identify the structure with a secondary allyl chloride corresponding to:

$$—CHCl—C(CH_3)=CH—CH_2— \quad \text{or} \quad —CH_2—C(CH_3)=CH—CHCl—$$

These rubber-allyl chlorides resemble Neoprene not only because of their reduced swelling in aliphatic hydrocarbons, but also in their mechanical properties; they differ, however, in their aging properties. This change in mechanical properties corresponds to the general effect exerted by a polar group. In an olefinic polymer it is accompanied by a higher limiting temperature of elasticity. As soon as the double bond disappears (as in hydrochlorides), even small concentrations of chlorine have a pronounced influence. Our findings, summarized schematically in Figure 8, are in good agreement with the recent results of American authors[45]. Figure 8 shows that partially hydrochlorinated NR remains plastic-elastic and soft until about 70–75 per cent of the double bonds are saturated; such polymers recover only slowly after elongation and show a strong tendency to crystallize[46]. The polymer finally becomes preponderantly crystalline and, therefore, a brittle powder.

Gutta-percha shows a generally similar behavior, but differs in two details. At the beginning of the hydrochlorination the spontaneous formation of crystals, typical for gutta, becomes inhibited and the polymer therefore now shows elastic recovery like that of NR. At the end of the hydrochlorination a lower

final value for the chlorine content in gutta is reached than in NR. The hydrochloride from polyisoprene shares the lower final value of 28 per cent of chlorine with gutta hydrochloride, but differs from it in mechanical properties; at room temperature it is elastic although it has a slow rate of recovery.

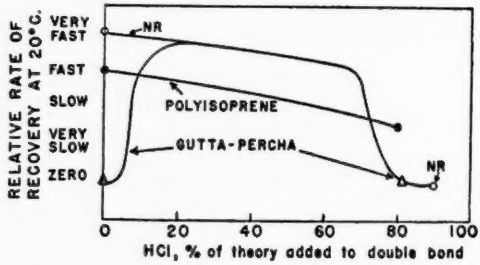


FIG. 8.—Influence of hydrochlorination on the mechanical properties of natural rubber, gutta-percha, and polyisoprene.

The difference between the hydrochlorides from NR and gutta, on the one hand, and polyisoprene, on the other hand, indicates the significance of a regular chain structure. The comparison between the tertiary and the allylic chlorides of NR serves to demonstrate the significance of the double bond. There exists, however, a third factor which determines the plastic-elastic properties of a paraffinic polymer: the energetical and geometrical symmetry of the molecular units; this will become clear from the following discussion.

GEOMETRICAL AND ENERGETICAL SYMMETRY

Polyvinyl compounds can be divided into two classes, which differ in their brittle points by as much as 100–200° (see Table VII).

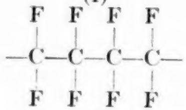
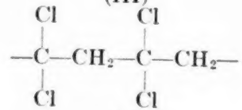
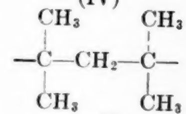
Group A.—This group consists of symmetrical molecules. These chains are highly flexible in the amorphous state, even at very low temperatures; in fact, the brittle point of Teflon seems to approach that of the hypothetical poly-1,4-butadiene. They show a great tendency to crystallize and structures (I–III) are therefore inelastic at ordinary temperatures—comparable to gutta-percha[47]. The absolute value of the brittle point depends on the amount of crystalline phase, as well as on structural details, *e.g.*, impurities and branching (II) and (III), or the bulkiness of the methyl groups in (IV).

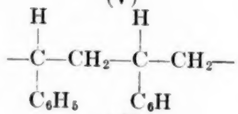
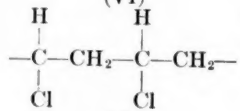
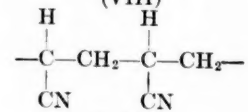
If sufficiently amorphous phase is present, the brittle point becomes only apparently independent of the crystalline fraction; actually very small changes in the latter are sufficient to raise the brittle point by as much as 50–100°. Polyethene becomes brittle when immersed in alcohol at room temperature[48], although this liquid shows very little interaction even with the amorphous phase of the polymer. Since this phenomenon is reversible, it is an indication of the existence of a limiting value of the ratio of amorphous to crystalline phases. A minute dilution with alcohol leads to weakening of the amorphous phase which is quite comparable to the reduced mechanical properties of weakly swollen elastomers under strain.

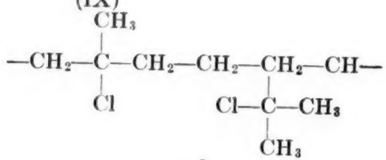
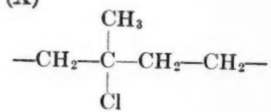
The introduction of softeners or copolymerization in Group A leads to reduction of the crystalline phase. Small quantities of softener in (III) produce lowering of the brittle point by nearly 200°, whereas the same quantity of softener in (VI) has only a moderate effect. This difference is more remarkable

TABLE VII

INFLUENCE OF STRUCTURE ON BRITTLE POINTS OF PARAFFINIC POLYMERS*

Group A No.	(I)	(II)	(III)	(IIIa)	(IV)
		—CH$_2$—CH$_2$—CH$_2$—CH$_2$—		III + 9% softener	
Brittle point (° C)	−80	−68.5	>+150 73% Cl	−25 67% Cl	−50

Group B No.	(V)	(VI)	(VII)	(VIII)
			(VI) +9% softener	
Brittle point (° C)	+80	+81 57% Cl	~+50° 52% Cl	>+150

Group C No.		(IX)		(X)
	{80% $C_5H_5 \cdot HCl$ {20% C_5H_6		{80–90% $C_5H_5 \cdot HCl$ {20–10% C_5H_6	
Brittle point (° C)		−3 29% Cl		>+90 (29–31% Cl)

* (I), Renfrew and Lewis[49]; (III) Mark[50] (II–VI); Boyer and Spencer[4]; (VIII–X), Salomon and Koningsberger[1].

because the chlorine content in (III) is higher than in (VI). An explanation can be deduced from a comparison of the physical properties of liquids with a symmetrical distribution of polar groups, like CCl_4 and $CCl_2{=}CCl_2$, with those of the $CHCl_3$ type. The latter exhibit a more pronounced tendency to associate with unlike molecules, as can be seen from their efficiency as swelling agents[35]. It is obviously the symmetrical structure of the molecular unit (III) which leads to internal compensation of the group moments, which in turn favors the ease of rotation in (III) when a softener is present (III*a*).

Group B.—The properties of this group, representing polymers with asymmetrical units, are very different. The polar and polarizable groups introduce strong intermolecular forces which are not compensated within the molecular unit. They therefore inhibit the easy formation of crystals, as well as the rotation of the flow units. The brittle point is not directly correlated to the strength of the dipole moment, but seems to depend mainly on the combination of electrical and geometrical asymmetry of the unit.

Methyl groups next to polar groups will tend to screen off the polar attraction and therefore lower the brittle point, *e.g.*, methylacrylonitrile has a measurable softening point whereas acrylonitrile decomposes before that point is reached. In other cases, however, the influence of methyl groups is comparable to that found with polymeric olefins. The brittle point of polymethyl acrylate is raised by methylation and the same conclusion must be drawn from a comparison of compounds (II) and (IV).

Group C.—We shall now consider once more the elasticity of polyisoprene hydrochlorides (see Table VII). The flexibility of the hydrochloride from synthetic polyisoprene (IX) is quite similar to that of a polyvinyl chloride with about 30–40 per cent of softener. The intermolecular attraction is obviously a direct function of the chlorine concentration (by volume). The mechanical strength, however, is higher in the polyisoprene derivative, due to the absence of low-molecular softeners.

The hydrochloride from NR (X) crystallizes readily at and above room temperature; in fact, when all traces of solvent are removed, the softening point is not far below the melting point of the crystals. Addition of 5–10 per cent of softener or solvent is sufficient to keep the material flexible far below 0° C. The essential difference between (IX) and (X), when comparing polymers with equal contents of chlorine and softener, is that (IX) becomes extensible and elastic, while (X) only becomes pliable. It is obvious that the strong tendency to crystallize, which pertains even in the swollen state[47], confers the film-forming properties on (X). The fact that a geometrically and energetically asymmetrical unit, like that in (X), exhibits such a strong tendency to crystallize is rather unexpected in the light of the data outlined in Table VII. Actually very specific steric conditions must be assumed for a full interpretation of this crystal structure[51].

VI. SOME GENERAL CONCLUSIONS

The position taken by NR within the general group of elastomers and plastics was outlined by Mark[52] some time ago. The larger variety of experimental evidence and broader range of temperatures discussed in the present paper now make possible a more detailed differentiation. One rather unexpected result emerges from the foregoing sections: structural factors of the diene, which are preferable from a kinetical point of view, produce undesirable mechanical properties in the polymer. Another experience is that a property

of matter which improves the applicability of the elastomer at high temperatures impedes its use under sub-zero service conditions. We shall attempt to untangle these complex correlations by stepwise discussion of a number of structural features.

Methyl groups.—The presence of methyl groups in the diene leads, in radical-initiated polymerization, to the preponderant formation of 1,4-addition products, but the ease of rotation in the resulting polymeric olefin is severely restricted; this in turn causes a considerable increase in the limiting temperature of elasticity. All polymers and copolymers from dienes with two or more methyl groups are, therefore, practically not elastic below 0° C. The combination of one methyl group with a polar or polarizable group leads to similar immobilization; consequently, development in the series of methylchloroprenes, as well as in that of copolymers from isoprene, is limited by this fundamental property.

1,2- and 3,4-additions.—Such additions reduce the flexibility of the chain to a degree quite comparable to that produced by methyl groups: properties of polyisoprene produced by alkali-metal catalysis are greatly influenced by this phenomenon; those of the corresponding polybutadiene are also determined by the large amount of 1,2-addition. Improvements, however, are within the realm of experimental possibilities[53].

Although copolymerization of butadiene with acrylonitriles may have a directing effect on 1,4-addition[54], it must be kept in mind that the favorable effect on the straight-chain structure is reached only at the cost of a higher limiting temperature of elasticity, comparable to that of two methyl groups. These structural limitations in mechanical properties and the fact that a reinforcing filler necessitates the presence of double bonds lead to the rather surprising conclusion that further development in the field of general-purpose elastomers can scarcely be expected from new combinations of monomers[55].

Straight-chain structure.—GR-S has been termed an elastically inverted[56] elastomer. It fails to recover quickly during repeated small deformations, thus contributing to the heat build-up, but does not yield sufficiently to large extensions, which causes the growth of cracks. The first-mentioned property has been attributed to the presence of phenyl groups, whereas the second one is clearly related to the irregular chain structure which produces another mechanism of retraction[57].

The inferior properties of isorubber indicate that a preponderantly straight chain without a prevailing *cis* structure will not lead to an elastical reversion of the GR-S type. Such partial improvement in straightness of a chain structure may even lead to a loss in favorable properties of GR-S without any gain.

Cis-structure and crystallization. It has been suggested that, even in the amorphous state, a *cis*-structure is superior to a *trans*-structure in elastic properties[58]. The *cis*-configuration in NR not only limits crystallization to a useful extent, but—even more surprising—the amount of crystals can be adjusted by vulcanization. In fact, this correlation is such a close one that crystallization is being used in the T-50 test as a measure of vulcanization. Neoprene, although it crystallizes, does not exhibit this correlation with the state of cure[59] and is, therefore, more difficult to adapt to service conditions at low temperatures.

The mechanical properties of NR at ordinary and higher tempeatures cannot be interpreted by the occurrence of crystallization alone[60]. A comparison with the properties of vulcanized gutta-percha suggests that the rate of

crystallization, as well as the orientation and the size of the crystallites, will be significant. Finally, at extremely high temperatures, the size of these crystals may diminish below the limiting value of x-ray identification.

SUMMARY

The correlation between structure and properties of elastomers prepared from dienes, natural rubber, gutta-percha, as well as those of some significant derivatives of natural rubber, are discussed. The similar influence exerted by methyl groups on the brittle point, elastic recovery, and permeability to gases is demonstrated and separated from the effect caused by insertion of $—CH_2—CHR—$ groups in straight-chain polybutadiene, which takes place during copolymerization or 1,2 addition. The preponderant influence of an unbranched-chain structure on tensile strength at elevated temperatures and in the swollen state is illustrated. Complex compounds with silver nitrate provide further evidence for the particular symmetry of the natural rubber chain: They are reinforcing agents for synthetic elastomers. The brittle points of hydrochlorides from natural rubber, gutta-percha, and polyisoprene are compared with those of polyvinyl compounds. Correlation between the structure of molecular units in a polymeric paraffin derivative and its elasticity is pointed out.

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REFERENCES

[1] Salomon and Koningsberger, *J. Polymer Science* **1**, 200, 364 (1946).
[2] Van Amerongen, *J. Applied Physics* **17**, 972 (1946).
[3] In Part V, to be published.
[4] Boyer and Spencer, in "Advances in Colloid Science", New York, **1946**, Vol. 2, p. 1.
[5] Liska, *Ind. Eng. Chem.* **36**, 40 (1944); RUBBER CHEM. TECH. **17**, 421 (1944).
[6] Borders and Juve, *Ind. Eng. Chem.* **38**, 1066 (1946).
[7] Marvel, Bailey, and Inskeep, *J. Polymer Science* **1**, 275 (1946).
[8] Schulz, *Ber.* **74**, 1766 (1941).
[9] Ziegler, Grimm, and Willer, *Ann.* **542**, 90 (1939).
[10] Yukubchik, Vasiliev and Zhabina *J. Applied Chem.* (U.S.S.R.) **17** 107 (1945); RUBBER CHEM. TECH. **18** 780 (1945).
[11] N. V. De Bataafsche Petroleum Mij; Netherlands patent 54,715.
[12] Salomon and Koningsberger *J. Polymer Science* **1**, 364 (1946). See Figs. 2 and 3.
[13] Hermans and van Eyk, *J. Polymer Science* **1**, 408 (1946).
[14] Salomon and Koningsberger, *J. Polymer Science* **1**, 200 (1946).
[15] Boonstra and Van Amerongen, Netherlands patent 58,427, and applications 114,305, 114,318 and 114,641.
[16] Davis, Goldblatt, and Palkin, *Ind. Eng. Chem.* **38**, 53 (1946).
[17] Van Amerongen, private communication.
[18] Field, Woodford, and Gehman, *J. Applied Physics* **17**, 386 (1946).
[19] Farmer, in "Advances in Colloid Science", New York, **1946**, Vol. 2, p. 302.
[20] Salomon and Koningsberger, *J. Polymer Science* **1**, 364 (1946). See Fig. 10.
[21] Harries, "Untersuchungen über die natürlichen and künstlichen Kautschukarten", Berlin, **1919**.
[22] McMillan, Bishop, Marple, and Evans, *India Rubber World* **113**, 663 (1946).
[23] Liska, *Ind. Eng. Chem.* **36**, 44 (1944); RUBBER CHEM. TECH. **17**, 421 (1944); Boyer and Spencer in "Advances in Colloid Science", New York, **1946**, Vol. 2, p. 1.
[24] Stöcklin, *Kautschuk* **19**, 3 (1943).
[25] Van Amerongen, *J. Applied Physics* **17**, 972 (1946); *J. Polymer Science* **2**, 381 (1947).
[26] Kistiakowsky, Lacher and Ransom, *J. Chem. Physics* **6**, 900 (1938).
[27] Kuhn and Kuhn, *Helv. Chim. Acta* **29**, 1095 (1946).
[28] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[29] Hoekstra, *Proc. Rubber Tech. Conf. London*, **1938**, p. 362.
[30] Hamm, Thesis, Delft, **1946**, p. 55.
[31] Whitby and Katz, *Ind. Eng. Chem.* **25** 1204, 1338 (1953); RUBBER CHEM. TECH. **7**, 40 (1934).
[32] Goppel, Thesis, Delft, **1946**.
[33] Arlman, J. J., private communication.

[34] Wildschut, "Technological and Physical Investigations on Natural and Synthetic Rubbers", Elsevier, New York and Amsterdam, **1946**, p. 153.
[35] Salomon and Koningsberger, *J. Polymer Science* **2**, 355 (1947).
[36] Somerville and Russell, *Ind. Eng. Chem.* **25**, 1096 (1933).
[37] Bunn, in "Advances in Colloid Science," New York, **1946**, Vol. 2, p. 134.
[38] Van Rossem and van der Meyden, *J. Soc. Chem.* **45**, 67T (1926).
[39] Kratky, Philipp, Posnansky, and Schossberger, *Naturwissenschaften* **26**, 123 (1938); RUBBER CHEM. TECH. **11**, 661 (1938).
[40] Winstein and Lucas, *J. Am. Chem. Soc.* **60**, 836 (1938).
[41] Goppel J. M. and Arlman, J. J., private communication.
[42] Baker, W. O., and Pape, N. R., Abstracts, 109th Meeting of Am. Chem. Soc., April, **1946**.
[43] Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114.
[44] Netherlands patent application 118,260 by the Rubber-Stichting.
[45] D'Ianni, Naples, Marsh, and Zarney, *Ind. Eng. Chem.* **38**, 1171 (1946).
[46] Gehman, Field and Dinsmore, *Proc. Rubber Tech. Conf. London*, **1938**, p. 961.
[47] Houwink, *British Plastics* **18**, 192 (1946).
[48] Richards, *Trans. Faraday Soc.* **42**, 27 (1946).
[49] Renfrew and Lewis, *Ind. Eng. Chem.* **38**, 870 (1946).
[50] Mark, in "The Chemistry of Large Molecules", New York, **1943**, p. 58.
[51] Bunn, *Proc. Roy. Soc. London* **A180**, 67 (1942); RUBBER CHEM. TECH. **15**, 731 (1942).
[52] Mark, *Ind. Eng. Chem.* **34**, 1343 (1942); RUBBER CHEM. TECH. **16**, 268 (1943).
[53] D'Ianni, Abstracts, 110th Meeting of Am. Chem. Soc. Sept. **1946**.
[54] Alekseeva, *Zhur. Obshchei Khim.* **11**, 353 (1941); RUBBER CHEM. TECH. **15**, 698 (1942).
[55] German research chemists quoted by Weidlein, *Chem. Eng. News* **24**, 771 (1946).
[56] Braendle and Wiegand, *J. Applied Physics* **15**, 304 (1944).
[57] Kuhn and Kuhn, *Helv. Chim. Acta* **29**, 1647 (1946).
[58] Bunn, *Proc. Roy. Soc. London* **A180**, 82 (1942); RUBBER CHEM. TECH. **15**, 742 (1946).
[59] Forman and Radcliff, *Ind. Eng. Chem.* **38**, 1048 (1946).
[60] Wildschut, *J. Applied Physics* **17**, 51 (1946).

SOME STRUCTURAL AND CHEMICAL ASPECTS OF AGING AND DEGRADATION OF VINYL AND DIENE POLYMERS *

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INTRODUCTION

The aging and degradation of polymeric substances by such agencies as heat, light, and oxygen have been the subject of very considerable and extensive research because of their great practical importance. The problem has, however, proved to be one of great complexity because of the simultaneous operation of several types of chemical reactions, each of which leads to different structural or chemical changes in the polymeric molecules. These in turn produce inordinately large effects on the physical properties of the substance in question. A complete understanding of the aging problem will of necessity invoke contributions from the organic chemist, the physical chemist, the physicist, and the engineer.

Despite the fact that our knowledge of the details is far from complete, some unified patterns of thought are, nevertheless, emerging which enable us to regard the problem in terms of certain unifying concepts. First, it has become increasingly clear that the chemical reactivity of vinyl and diene polymers manifested during aging and degradation is similar to the reactivity manifested during polymerization: namely, the activated intermediates are radicals and the reaction proceeds by a chain mechanism. Second, the important changes in mechanical properties occurring during aging are the result of concurrent aggregative processes (further polymerization, branching, cross-linking, cyclization) and disaggregative processes (scission, depolymerization). For simplicity we shall refer to these processes as cross-linking and scission. Important changes in mechanical properties may often occur before any important chemical changes have taken place as measured, for example, by chemically absorbed oxygen. Finally, chemical changes, such as change of unsaturation or evolution of degradation products, may also be explained by the same general radical mechanisms.

Certain polymer properties, such as light transmission and electrical power factor, are in some cases extremely sensitive to chemical changes, such as the formation of conjugated double bonds, oxygenated polar linkages, and the like.

The initial stage in the process of aging or degradation is probably the formation of a hydrocarbon free radical by abstraction of a hydrogen atom some place along the polymeric chain. This may occur either by the action of a free radical left over from the polymerization process, *e.g.*, a catalyst molecule or fragment, or by the direct action of oxygen. Light acting on a photosensitive molecule can also produce a radical fragment which can be transferred to the polymer chain by abstraction of a hydrogen atom.

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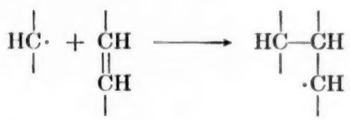
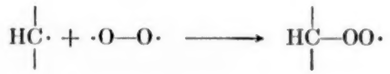
We shall refer to the polymer free radical, whose active odd electron can be any place along the polymer chain including the ends, as the radical, R·. This radical in general readily adds O_2 when the latter is present to give the radical, $RO_2\cdot$. Finally, $RO_2\cdot$ undergoes a chain-transfer reaction with an inactive portion of a polymer chain by abstracting a hydrogen atom to form the hydroperoxide, ROOH, and leaves behind another radical of the type, R·

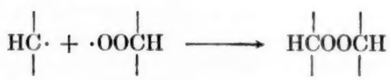
These three active species, R·, $RO_2\cdot$, and ROOH, are probably responsible for a large share of the deteriorative processes that we have labeled as concurrent aggregative and disaggregative reactions. Mechanisms for these processes have been proposed in the literature and will be discussed below.

Aggregative Processes


(1a)


(1b)


(1c)


(1d)


(1e)


(1f)

Disaggregative Processes

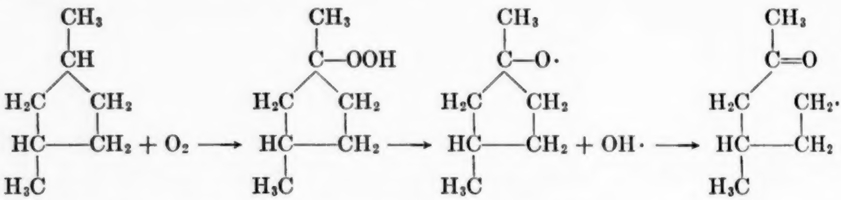
$$-CHX\dot{C}HCHXCH_2- \longrightarrow -CHXCH{=}CHX + \cdot CH_2- \quad (2a)$$
$$-CHXCH_2CHXCH_2OO\cdot \longrightarrow -CHXCH_2\cdot + CH_2O + CHXO \quad (2b)$$
$$-CHXCH_2CHXCH(OO\cdot)CHX- \longrightarrow -CHXCH_2\cdot + CHXO + CHOCHX- \quad (2c)$$
$$-CHXCH(OOH)CHXCH_2- \longrightarrow -CHXCHO + \cdot CHXCH_2- + \cdot OH \quad (2d)$$

Under certain conditions, some of these reactions are presumably more important than others. For example, reaction (2a) is probably most important at high temperatures where large-scale depolymerization takes place. At lower temperatures, degradative reactions probably involve oxygen more directly as in reactions (2b), (2c), and (2d). The relative rates of aggregative and disaggregative reactions depend on the chemical nature of the polymer and on the conditions of aging. For example, as we shall discuss shortly, methyl side groups appear to favor scission, and carbon-carbon double bonds in the hydrocarbon chain favor cross-linking.

The concurrence of aggregative and disaggregative processes and the importance of oxygen were suggested by various workers, including Spence and Ferry[1], Staudinger[2], Schulz[3], Stevens[4], and Taylor and Tobolsky[5]. The chain

characteristics of depolymerization were first suggested by Chalmers[6], who stated that "the decomposition of high polymers has many features which suggest the existence of a chain mechanism of an inverse character to that involved in their generation".

The various mechanisms whereby oxygenated radicals and hydroperoxides are formed and their subsequent aggregative and disaggregative reactions are discussed in a wide variety of papers—many on specialized topics. Farmer and Sundralingam[7] were among the first to emphasize the importance of hydroperoxides, particularly on the α-methylene carbon atoms in olefinic substances, and proposed various mechanisms for subsequent secondary reaction involving the hydroperoxide. George and Walsh[8] give the following explanation for the oxidation of 1,3-dimethylcyclopentane:



The open-chain free radical formed can then stabilize by various processes, *e.g.*, abstracting a hydrogen atom from another molecule.

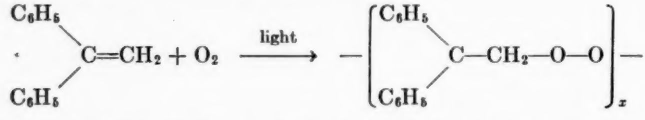
Medvedev and Zeitlin[9] in recent studies have shown that polymerization of styrene in the presence of oxygen gave rise to a constant ratio between oxidized and polymerized products. They suggest a radical chain mechanism for both which essentially involves the following reactions:

$$\text{—CHXCH}_2\text{CHXCH}_2\text{CHXCH}_2\cdot \longrightarrow \begin{cases} \xrightarrow{\text{O}_2} \text{—CHXCH}_2\text{OO}\cdot \\ \xrightarrow{\text{CH}_2\text{=CHX}} \text{polymerization product} \end{cases}$$

$$\text{—CHXCH}_2\text{CHXCH}_2\text{CHXCH}_2\text{OO}\cdot \longrightarrow \text{—CHXCH}_2\text{CHXCH}_2\cdot + \text{CHXO} + \text{CH}_2\text{O}$$

$$\text{—CHXCH}_2\text{CHXCH}_2\text{CHXCH}_2\text{OO}\cdot + \text{CH}_2\text{=CHX} \longrightarrow$$
$$\text{—CHXCH}_2\text{CHXCH}_2\text{CHXCH}_2\text{OOCHXCH}_2\cdot$$

The inactivity of the $RO_2\cdot$ radical as far as further addition of monomer is concerned is pointed out by the work of Barnes[10] on the inhibition of the photopolymerization of vinyl acetate and methyl methacrylate by oxygen, and also by the well-known inhibitory effect of oxygen in emulsion polymerization[11]. Apparently the $RO_2\cdot$ radical usually tends to degrade or undergo chain transfer (to form a hydroperoxide), although a notable exception occurs in diphenylethylene according to the work of Staudinger[12]:



Another indication that $RO_2\cdot$ tends preferentially to undergo disaggregative reactions can be inferred from the work of Stevens[13], in which he showed

that photogelation of natural rubber occurs in the virtual absence of oxygen, whereas degradation occurs in the presence of oxygen. Also, GR-S, which generally tends to harden when heat-aged in an air oven, sometimes shows signs of softening when aged in an oxygen bomb. This indicates that R· tends to undergo cross-linking reactions, but that $RO_2\cdot$ and ROOH (which are present in larger amounts under high pressures of oxygen) tend to show disaggregative reactions.

In spite of certain general statements and facts, such as those mentioned above, the exact mechanisms and relative rates of the various reactions which R·, $RO_2\cdot$, and ROOH undergo are still not known. It is hoped that precise studies, such as have been made on relative rates of addition of radicals to double bonds (in copolymerization studies by Mayo and Lewis[14], Alfrey and Goldfinger[15], and others, and rates of chain transfer[16]), will eventually be extended to all radical reactions.

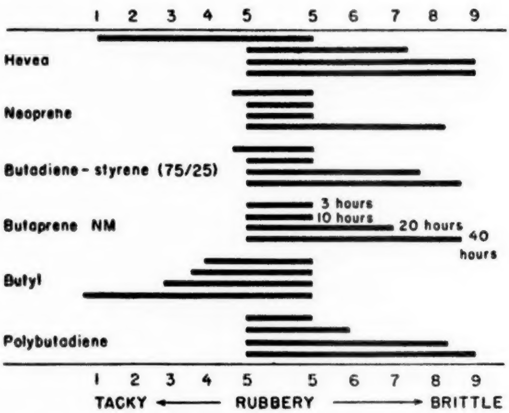


FIG. 1.—Appearance of thin gum stocks after aging at 150° C.

As stated previously, the aging of polymeric material such as rubber at elevated temperatures is the result of two processes taking place simultaneously: (1) cross-linking and (2) scission of the molecules. Cross-linking hardens the rubber; scission causes the rubber to become soft and tacky. The two reactions occur simultaneously, and the actual change in physical characteristics of any given rubber depends on the net result of the two reactions and, therefore, on their relative rates.

A general survey of the magnitude of the aggregative (cross-linking) and disaggregative (scission) reactions occurring during the heat-aging of rubber polymers may be presented in a very simple way, as shown in Figure 1. Thin samples of Hevea, Neoprene, butadiene-styrene (75/25), Butaprene-NM, Butyl and polybutadiene gum stocks were aged in an air oven at 150° C. At definite intervals of time (after 3, 10, 20, and 40 hours), the rubber samples were removed and given an empirical hardness test. Each polymer on removal from the oven was graded from 1 to 7 on the basis of its physical appearance (number 1 indicated extreme tackiness, 4 normal rubberiness, and 7 extreme hardness). It was always observed that Butaprene, Neoprene, and the butadiene-styrene polymers became brittle with aging, indicating the cross-linking reaction to be more preponderant than the scission reaction. Butyl

rubber was observed to become more tacky with aging, indicating that in this case scission was most preponderant. On the other hand, Hevea rubber, during the first few hours of heat-aging, became extremely tacky, and then gradually approached complete brittleness.

It should be noted that any single physical test does not suffice to characterize completely the results of aging. For example, samples that harden during aging may show an increasing tensile strength and decreasing elongation at break, whereas the reverse may be true for samples that soften during aging.

SIMULTANEOUS POLYMERIZATION AND DEGRADATION

If polymerization and degradation are presumed to occur by means of the same radical mechanism, one should expect that under certain experimental conditions both reactions can be shown to occur simultaneously[17].

Experiments of this kind are shown, for example, in Figure 2. In this case, solutions of monostyrene and polystyrene in toluene (concentration, 16 g. per 100 cc.) were prepared and placed in 500-cc. flasks fitted with reflux condensers.

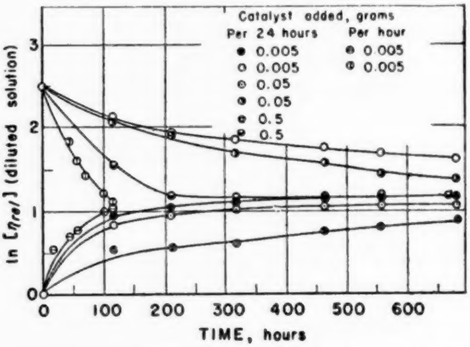


FIG. 2.—Polymerization degree *vs.* time: concentration of styrene in toluene, 16 g. per 100 cc.; solutions refluxed at 111° C.

About 350 cc. of solution was placed in each flask, and the flasks with attached condensers were set over hot plates in beakers of petroleum oil. Altogether four monomer solutions and four polymer solutions, each in separate flasks, were refluxed, the refluxing temperature being close to 111° C in every case. To one flask containing monomer solution and to another containing polymer solution, 0.005 gram of benzoyl peroxide was added every 24 hours (0.01 per cent based on the weight of styrene). To another set—monomer and polymer solutions—0.05 gram of benzoyl peroxide (0.1 per cent) was added every 24 hours. To a third set, 0.5 gram of benzoyl peroxide (1.0 per cent) was added every 24 hours; and finally, to the fourth set, 0.005 gram of benzoyl peroxide was added every hour. At periodic intervals of time, a few cubic centimeters of refluxing solution was withdrawn, diluted fourfold, and viscosity measurements were performed.

As is clear from Figure 2, the relative viscosity of the monostyrene solution to which 0.005 gram of catalyst had been added every 24 hours, and the relative viscosity of the polystyrene solution to which 0.5 gram of catalyst had been added every 24 hours, both approach nearly the same steady-state viscosity, which was attained after thirteen additions to each solution. This same steady-

state value was attained by the monostyrene and polystyrene solutions to which 0.005 gram of catalyst was added every hour after 110 additions. It should be noted, however, that the total time elapsed in this last experiment was longer than that shown in Figure 2, because the solutions were kept refluxing overnight and during week ends, while no additions of catalyst were made. Since each flask contained 48 grams of mono- or polystyrene in solution, it is clear from these results that a steady-state value of the viscosity can be reached by addition of as little as 1 per cent total catalyst in the case of the polymer solution, and by the addition of even less catalyst in the case of the monostyrene solutions.

For the polystyrene solution, slow addition of small amounts of benzoyl peroxide resulted in a very slow fall in viscosity. On the other hand, in the case of the monomer solution, addition of large amounts of catalyst retarded the approach to the steady-state value considerably.

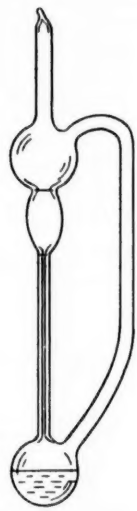


FIG. 3.—Reversible viscometer.

Since the molecular weight of a polymer determines its viscosity in solution, it is apparent from this experiment that polymerization catalysts—such as benzoyl peroxide—which decompose to free radicals may also catalyze degradation.

Experiments are now in progress designed to follow the molecular-weight changes of polymerized and degraded styrene by viscosimetric, osmotic pressure, and light-scattering methods. The results of these precise studies will be published in a subsequent article.

Further experiments to show the existence of simultaneous polymerization-degradation reactions of styrene in toluene solutions under variable conditions of light, heat, air, catalysts, and photosensitizers were successfully performed by observing the changes in solution viscosity by means of the sealed Pyrex reversible viscometers shown in Figure 3. Solutions of styrene in toluene could easily be placed in the viscometer, which is then sealed off in air, *in vacuo*, or in the presence of any desired gas. In all cases, relative viscosity was defined

as the time of flow for the solution at 25° C between the two marks shown, as compared to the time of flow for the solvent.

Studies on polymerization-degradation of styrene solutions in the presence of light and air at 100° C are shown in Figure 4. In this experiment, purified styrene containing 0.01 gram of benzoyl peroxide to 8.82 cc. of styrene was placed in test-tubes, which were sealed off in air. The sealed tubes were placed in an air oven at 100° C, and heated for various lengths of time—5 minutes, 20 minutes, 45 minutes, 1 hour, 3 hours, 5 hours, and 9 hours. The products ranged from very fluid liquids to viscous liquids, plastic liquids, soft plastics, and finally very hard plastics. These materials were obviously mixtures of monomer and polymer. After removal from the oven, the contents of each tube were immediately dissolved in sufficient toluene to make up a solution of 16 grams per 100 cc.; 8-cc. portions of each solution were then placed in reversible viscometers and sealed in air. The viscometers were placed on an asbestos board and were simultaneously exposed to the light of an S-1 sun lamp 5 inches away. The steady-state temperature that was attained at the level of the viscometer bulbs was 100° C. Under the combined effects of heat, light, and air, the relative viscosities of these solutions began to change as shown in the graph (Figure 4) until a steady state was reached. It is interest-

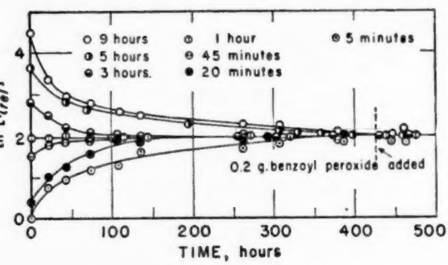


FIG. 4.—Polymerization degree *vs.* time: concentration of styrene in toluene, 16 g. per 100 cc.; catalyzed by light at 100° C.

ing to note that the viscosity of the 1-hour solution did not vary appreciably during the entire course of the experiment.

Experiments of the type just mentioned were repeated but this time the viscometers were sealed off *in vacuo*. The pressure of air in the viscometers was in all cases less than 10^{-5} mm. of mercury. The results of this experiment are shown in Figure 5. It is clear that the rate of increase of relative viscosity for the styrene solutions of lowest polymerization degree was almost unaffected by the exclusion of oxygen. The same steady states were reached *in vacuo* as in the presence of air by the styrene solutions—for which the styrene had been polymerized for 15 minutes, 30 minutes, 90 minutes, 3 hours, and 7 hours. However, the styrene, which had been polymerized for 12 hours until it was a hard plastic with undoubtedly very little monomer left, did not degrade at an appreciable rate in the absence of air, although it had reached a steady state under the effects of heat and light when oxygen was present.

Two special runs were then made, the results of which are also shown in Figure 5. In the first case, 0.05 gram of diphenyl ketone (a photosensitizer) was added to the 12-hour styrene solution and the solution was sealed off in the absence of oxygen. In the second run, a solution was made up which contained 6 parts of the 12-hour styrene and 1 part of the 15-minute styrene. This too

was sealed *in vacuo* and exposed to heat (130° C) and light. The results are shown in Figure 5. The polystyrene solution with photosensitizer added showed peculiar behavior in that for a time the viscosity showed little tendency to drop, but suddenly there was a very rapid decrease and an approach to the steady-state value. The solution containing the mixture of 12-hour styrene and 15-minute styrene (which must have contained much monomer) first showed a marked increase in viscosity and then a decrease to the common steady-state value reached by the other solutions. It would appear that light of the wave lengths used (greater than 3000 Å.) can activate the monomer but not the polymer. The eventual falling off of viscosity is believed to be due to the reaction between an active monomer and a polymer molecule, causing transfer of activity to the polymer. The activated polymer molecule formed could then undergo a series of disaggregative or self-disproportionating reactions.

It is interesting to note that the steady-state relative viscosities obtained in the sealed viscometers were very much lower than the steady-state relative viscosities (measured undiluted) that were obtained in the refluxing solutions. No conclusive results have as yet been reached regarding the effect of temperature or light intensity upon the value of the steady-state viscosity obtained.

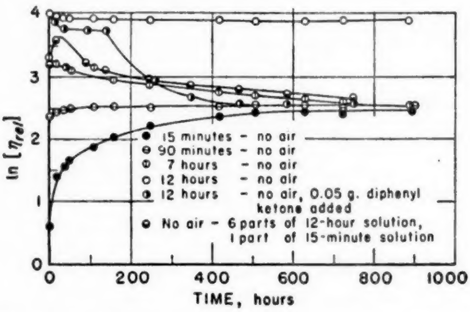


FIG. 5.—Polymerization degree *vs.* time: concentration of styrene in toluene, 16 g. per 100 cc.; catalyzed by light at 130° C.

Finally, to see whether the same effects of steady-state viscosity values could be observed in another polymer–solvent system, methyl methacrylate of varying degree of polymerization was prepared. 8.6-cc. portions of purified methyl methacrylate, with 0.02 gram of benzoyl peroxide dissolved, were sealed in Pyrex test-tubes and heated in an air oven at 90° C for 15 minutes, 45 minutes, and 3 hours. The contents of these tubes were then dissolved in sufficient acetone to give solutions of concentration equal to 16 grams per 100 cc. These solutions were then placed in reversible viscometers which were sealed in air and placed in an air oven at 90° C. To one viscometer containing 8 cc. of the "15-minute solution", 0.005 gram of benzoyl peroxide was added intermittently, as shown in Figure 5. Another viscometer containing the 15-minute solution was left unopened, as was also the viscometer containing the 45-minute solution. One viscometer containing the 3-hour solution was left unopened, whereas 0.005 gram of benzoyl peroxide was added occasionally to another viscometer containing this same solution. The results are shown in Figure 6. It is clear that the 15-minute solution to which no catalyst had been added, and the 45-minute and 3-hour solutions to which peroxide was added, approach the same steady-state viscosity. The viscosity of the 3-hour solution to which no cata-

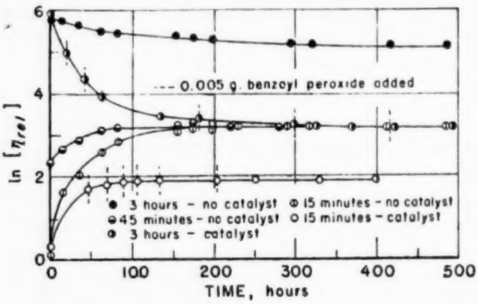


FIG. 6.—Polymerization degree *vs.* time: concentration of methyl methacrylate in acetone, 16 g. per 100 cc.; heated at 90° C.

lyst had been added did not drop appreciably. The viscosity of the 15-minute solution to which catalyst had been added leveled off to a lower apparent steady-state value than was reached by the other solutions. Previous experience with polystyrene solutions would seem to indicate that this solution could be brought to the viscosity level of the others only by continued addition of large amounts of catalyst.

ANALYSIS OF CONCURRENT AGGREGATIVE-DISAGGREGATIVE REACTIONS

The experiments discussed thus far have dealt generally with the overall effect of concurrent aggregative and disaggregative reactions on the heat-aging of rubber polymers and of styrene in toluene solutions. It is possible, however, by various physical methods, both to isolate and to measure separately the rate of one of these two concurrent reactions in the presence of the other. For example, one method that has been used to measure the extent of the scission reaction in the presence of the cross-linking reaction is the method of continuous stress relaxation, whereas intermittent stress relaxation measures the sum of the cross-linking and scission reactions[18]. Studies of the sol-gel content and viscosity changes of aging rubber polymers give indications of the net effect of aggregative and disaggregative reactions. It is possible also to measure the scission reaction alone by aging the polymer in dilute solutions and following the viscosity changes. Under this latter condition, the chains of the polymer are sufficiently far enough apart so that, during aging in solution, cross-linking between chains is largely repressed and only the scission reaction is effective.

It is interesting to note that oxygen must generally be present for cross-linking and scission to occur. Under certain conditions, however, chemical agents of various types can either retard or accelerate cross-linking and scission under conditions of heat aging. Thus it is possible to retard the heat-hardening, which is one of the great disadvantages of GR-S in practical service, by the inclusion of certain chemical agents in the rubber.

Figure 7 shows the effect of the addition of two different chemical agents to GR-S unstabilized latex, as measured by changes in gel per cent and swelling index during subsequent heat aging of the coagulated polymer. The latex containing added chemical agent was coagulated with salt and acid, and stripped of unreacted monomer. Samples of the polymers were then heat-aged in an air oven at 100° and 130° C. After 1, 3, 7, and 24 hours of aging at both temperatures, the samples were removed and measurements of percentage of

gel and swelling index were made. Similar studies, also shown in Figure 7, were made with a completely unstabilized polymer (the control) and with a sample of Hevea smoked sheet. These measurements were carried out in the conventional manner. Accurately weighed samples of the aged polymer were placed in a flask, covered with benzene, and allowed to stand for 48 hours in a dark cabinet. The benzene–polymer solution (consisting now of sol and swollen gel) was filtered through a wire screen. The amount of gel present was weighed; the amount of polymer in the gel was obtained from the difference between the weight of polymer in the sol and the original amount of rubber. The weight of polymer in the sol is obtained by evaporating to dryness an aliquot portion of the sol. Since the original amount of polymer used is known, the amount of polymer in the gel can then be determined. The ratio of the weight of polymer in the gel to the total original weight of polymer (×100) is the percentage of gel. The swelling index is the ratio of the weight of the gel to the amount of polymer in the gel. Thus the term *loose gel* would signify a gel with a high swelling index, *i.e.*, containing much solvent and little polymer, whereas a *tight gel* is highly cross-linked and contains little solvent.

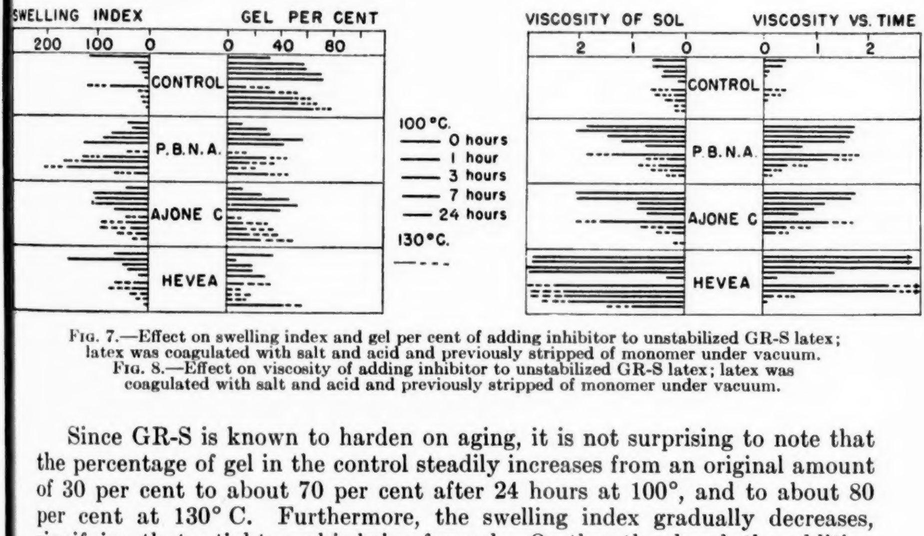


FIG. 7.—Effect on swelling index and gel per cent of adding inhibitor to unstabilized GR-S latex; latex was coagulated with salt and acid and previously stripped of monomer under vacuum.
FIG. 8.—Effect on viscosity of adding inhibitor to unstabilized GR-S latex; latex was coagulated with salt and acid and previously stripped of monomer under vacuum.

Since GR-S is known to harden on aging, it is not surprising to note that the percentage of gel in the control steadily increases from an original amount of 30 per cent to about 70 per cent after 24 hours at 100°, and to about 80 per cent at 130° C. Furthermore, the swelling index gradually decreases, signifying that a tighter gel is being formed. On the other hand, the addition of 2 per cent of P.B.N.A. (phenyl-β-naphthylamine) and 1 per cent of Ajone-C (2,2,4-trimethyl-6-phenyl-1,2-dihydroquinoline) tends to decrease the amount of gel formed and increase the swelling index.

The percentage of gel of Hevea smoked sheet decreased during the first few hours of aging and then gradually increased in the later stages of aging at 100° and 130° C. Also, the swelling index increased and then decreased below the original value. These aging characteristics agree well with the qualitative results shown in Figure 1, from which it is observed that Hevea rubber became initially tacky during aging at 150° and later approached brittleness.

Figure 8 shows the changes in the viscosity of the sol during the aging process described above. These changes are illustrated under the heading entitled "viscosity of sol". Viscosity measurements in an Ostwald viscometer were made on the soluble portions of the polymers used for the percentage gel

and swelling index studies. The numerical values given represent the natural logarithm of the relative viscosity divided by the concentration of rubber (in grams per 100 cc. of solution). The sol viscosity shows an expected decrease during aging, inasmuch as the gel preferentially extracts the larger molecules in the benzene-soluble portion. The data presented so far in Figures 7 and 8 show, in a general way, the overall effect of cross-linking and scission reactions on the aging of GR-S and Hevea polymers in the solid state. The cross-linking reaction may be isolated from the scission reaction by aging in solution. The second column in Figure 8 (viscosity *vs.* time) represents the change in viscosity of solutions of the same polymers during aging at 100° and 130° C. Solutions of the unaged polymer were placed in reversible viscometers of the type described in Figure 3. The viscometers were then sealed off in air and placed in the ovens at the two different temperatures, 100° and 130°. The solvent used was benzene. The numerical data were calculated by taking the logarithm of the relative viscosity. As was previously pointed out, these viscosity values cannot be considered absolute.

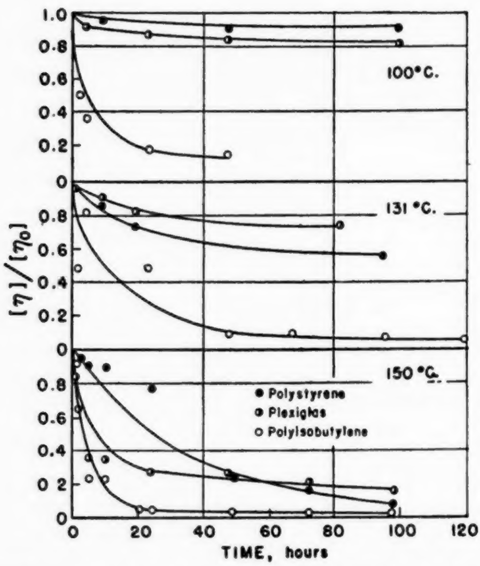


FIG. 9.—Change in intrinsic viscosity of various plastics during heat aging.

Under the influence of air and heat, the viscosities of all the polymers decreased with time. From the graph (Figure 8), it is evident that the chemical agents were effective in retarding the scission process, as measured by the viscosity changes.

Figure 9 shows some preliminary results of heat-aging studies of vinyl polymers. Thin films of polymethyl methacrylate, polystyrene, and polyisobutylene were aged at 100°, 131°, and 150° C in an air oven. At periodic intervals of time, small portions of the films were removed, and the intrinsic viscosity of each of the three polymers was determined. In Figure 9 the ratio of the intrinsic viscosity of the aged polymer to the intrinsic viscosity of the unaged polymer is plotted against linear time. It is to be noted that the

intrinsic viscosity is an index of the molecular weight of the polymer. Since in all three cases the intrinsic viscosity decreased with time of aging and no gel was formed, it is apparent that scission was preponderant. The polyisobutylene film showed the greatest relative change in intrinsic viscosity during aging.

In addition to following scission and cross-linking reactions by classical methods of molecular-weight changes, the reactions in polymers that occur at elevated temperatures may be separated, and the relative extent of each one studied independently by continuous and intermittent stress relaxation experiments. When a sample of rubber is extended to a fixed elongation and exposed to air at an elevated temperature, the relaxation of stress of the stretched sample measures only the extent of scission that is occurring. Any cross-links that are formed occur in a relaxed state relative to the constant elongation at which the sample is maintained. On the other hand, when the rubber sample is kept in a relaxed state and stretched only for short periodic measurements of stress, the variation in stress with time measures the sum of both the cross-linking and the scission reactions. The relative rates of continuous stress relaxation for various hydrocarbon rubbers at 100° C are shown in Figure 10.

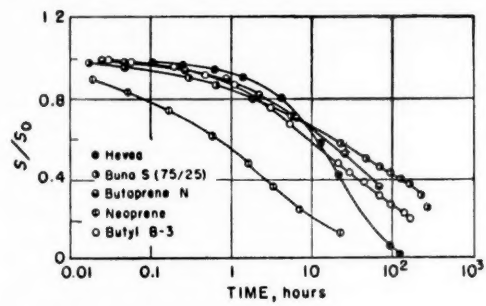


FIG. 10.—Relaxation of stress at constant (50%) elongation for various gum stocks at 100° C.

Stress divided by initial stress is plotted against logarithmic time. It is observed that Neoprene and Hevea rubber relax the fastest; GR-S and Butaprene-NM relax the slowest; Butyl is intermediate. Although the curves are not shown in this graph, the rates of relaxation of polyester and Lactoprene elastomers would be very much slower (about a hundredfold) than those of these hydrocarbon rubbers. For Hevea and Butyl, the stress, when measured intermittently, decreases with time, whereas for GR-S the stress increases. It is to be noted that both Hevea and Butyl become soft and tacky when exposed to air at elevated temperatures, whereas GR-S vulcanizates harden and become brittle. This gives a clear indication that the cross-linking reaction is faster than the scission reaction for GR-S, and *vice versa* for Hevea and Butyl. In general, it appears that double bonds in the hydrocarbon chain enhance both the cross-linking and the scission reactions, but favor the cross-linking reaction slightly. On the other hand, the presence of methyl side groups, as in Hevea or Butyl rubbers, seems to favor scission more.

The rates of continuous and intermittent stress relaxation at 130° C for GR-S and Hevea rubbers are given in the graphs in Figures 11 and 12. It is also possible to predict the extent of permanent set from these data since the rates of scission and cross-linking are obtainable from the rates of continuous

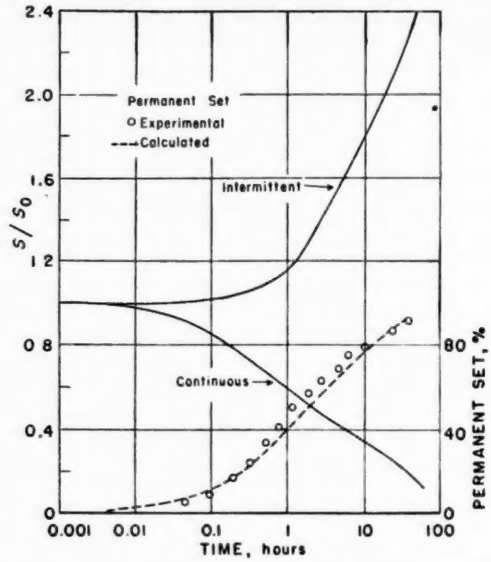


FIG. 11.—Calculation of permanent set from rates of continuous and intermittent stress relaxation for GR-S at 130° C and 50% elongation.

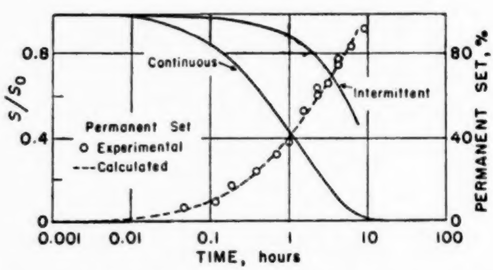


FIG. 12.—Calculation of permanent set from rates of continuous and intermittent stress relaxation for Hevea rubber at 130° C and 50% elongation.

and intermittent stress relaxation[19]. A comparison of experimentally observed permanent set with calculated permanent set is given in Figures 11 and 12 and shows excellent agreement.

STUDIES OF OXYGEN ABSORPTION

For a complete understanding of the mechanism and rate of oxidation of polymers it is necessary to study at least the following variables: (1) the rate of scission by continuous stress-relaxation studies or by periodic measurements of the decrease in viscosity of a dilute solution exposed to degradative conditions; (2) the net rate of scission and cross-linking, as measured by intermittent stress relaxation or by periodic measurements of sol–gel ratios, gel swelling index, and sol viscosity of the solid polymer exposed to degradative conditions; (3) the analysis of the products of oxidation; and (4) the rate of absorption of oxygen.

It has been postulated that the concurrent aggregative and disaggregative reactions involved in the heat aging of polymers proceed by a radical mechanism. On the basis of a radical mechanism involving R·, RO_2·, and ROOH, further studies should be directed toward developing a kinetic scheme for the rate of oxidizability of rubber and other polymers. Although many interesting attempts have been made to interpret the kinetics of oxygen absorption of various hydrocarbons, the most comprehensive studies appear to be those recently reported by Bolland and Gee[20]. Their work was confined specifically to small chain molecules. They found that the rate of oxygen absorption of ethyl linoleate could be expressed thus:

$$-d[O_2]/dt = K_a[RH][ROOH]\phi(p)$$

where:

$$1/\phi(p) = (1 + \lambda[RH]/p)$$

where RH signifies ethyl linoleate, ROOH represents the concentration of hydroperoxide formed during reaction (which can be accurately determined during reaction), p represents the constant pressure of oxygen that was maintained in the system, and λ and K_a are empirical constants. As can be seen, the rate of oxygen absorption is independent of oxygen pressure at high pressures, but becomes first order with respect to oxygen pressure at low pressures.

Bolland and Gee explained their results by means of the following kinetic scheme (a chain reaction involving the ethyl linoleate radical, R·):

Chain initiation	2 ROOH	$\xrightarrow{k_1}$	R·
Propagation	R· + O_2	$\xrightarrow{k_2}$	RO_2·
	RO_2· + RH	$\xrightarrow{k_3}$	ROOH + R·
Termination	R· + R·	$\xrightarrow{k_4}$	R—R
	R· + RO_2·	$\xrightarrow{k_5}$	ROOR
	RO_2· + RO_2·	$\xrightarrow{k_6}$	ROOR + O_2

When the oxygen pressure, p, is low, the last two equations may be neglected as terminating steps. Solving the equations by the steady-state method:

$$-d[O_2]/dt = k_2(k_1/k_4)^{1/2}[ROOH][O_2]$$

If p is large, the first two termination equations may be neglected. Then:

$$-d[O_2]/dt = k_3(k_1/k_6)^{1/2}[ROOH][RH]$$

In this treatment, it is assumed that sufficient hydroperoxide has been built up so that the rate-controlling initiation step is decomposition of the hydroperoxide into radicals. At the very early stages of oxidation, the rate-controlling chain initiation step may be the formation of radicals by the direct attack of molecular oxygen on the ethyl linoleate.

The decomposition of the hydroperoxide, studied separately, was found to be bimolecular. The energy of activation of the rate constant, k_1, was 26 kcal. By reasonable consideration, limits could be found for the activation energies

of all the steps. For example, E_2 was shown to be approximately zero and E_3, approximately 4.5 kcal.

The benzoyl peroxide-catalyzed oxidation of ethyl linoleate also was studied. It was found that the rate of initiation, which was formerly $k_1[ROOH]^2$, was now $k_7[BzO_2]$, for which the rate of decomposition of benzoyl peroxide could be separately studied. The rate of oxidation for peroxide-catalyzed oxidation of ethyl linoleate could be obtained from the previously derived expressions for autoxidation of ethyl linoleate merely by replacing $k_1[ROOH]^2$ by $k_7[BzO_2]$.

This excellent work on the oxidation of ethyl linoleate may well serve as a prototype of many more investigations of small and large molecules.

A comparative study of the rate of oxygen absorption of a large number of polymer types was undertaken in this laboratory to evaluate the factors affecting oxidation. It must be realized, however, that the conclusions drawn are limited by the fact that oxygen absorption alone is not a complete index of aging.

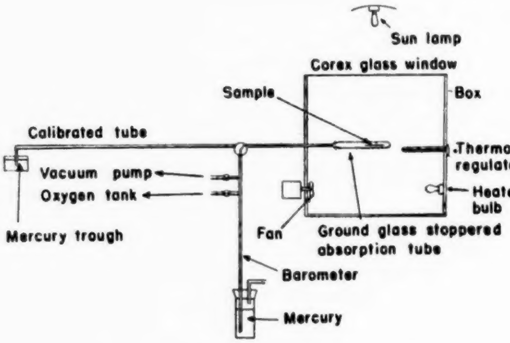


FIG. 13.—Oxygen absorption apparatus.

A problem of interest is that of specifying the determining factors which influence the comparative rate of oxygen absorption in different polymeric materials. We should like to present evidence to show that these factors may be specified by the following: (1) chemical structure of the polymeric material, (2) presence of antioxidants, and (3) vulcanization—mainly applicable to rubberlike materials that are prepared by different conditions of compounding and curing.

A unit of the apparatus used to study the rate of oxygen absorption is shown in Figure 13. Seven such units are employed in one experiment simultaneously. The sample holder consists of a Pyrex glass tube of 20-mm. bore attached to a horizontal tube of 3-mm. bore and 100-cm. length by means of a ground glass joint. The open end of the small tube is bent at right angles and dips into a mercury trough. The rubber sample is placed in the Pyrex tube, and exposed to heat and oxygen, or to heat, light, and oxygen, in an air oven. To hold the heat in the box and yet allow light to enter, the door of the box is fitted with a Corex glass window, which is quite transparent both to visible and ultraviolet light. As the absorption of oxygen progresses, mercury flows along the small horizontal tube and the distance of flow is measured. To convert the readings into cubic centimeters, each tube is carefully calibrated at a number of points by filling it with mercury to specified lengths and weighing the different amounts of mercury. Since changes in atmospheric pressure

affect the readings, a blank tube (the control) is always maintained under similar conditions and its readings are compared with those of the tubes in service. While oxygen absorption occurs, the oxygen pressure in the apparatus remains constant, because of the horizontal positions of the calibrated tubes. To carry out the experiments in the presence of pure oxygen rather than air, the absorption tubes are first evacuated before leading in the oxygen. A specified amount of Ascarite was placed in each absorption tube to remove any carbon dioxide or water vapor that might be formed, but no agent for carbon monoxide removal was provided. In all cases, samples with very high surface-to-volume ratios were used to eliminate the diffusion problem.

EFFECT OF CHEMICAL STRUCTURE ON RATE OF OXYGEN ABSORPTION

To compare the amount of oxygen absorption in various polymers, a run was carried out at 130° C on several rubber gum stocks in the absence of light. Figure 14 shows the oxygen absorption of Hevea, Butaprene-NM, Neoprene,

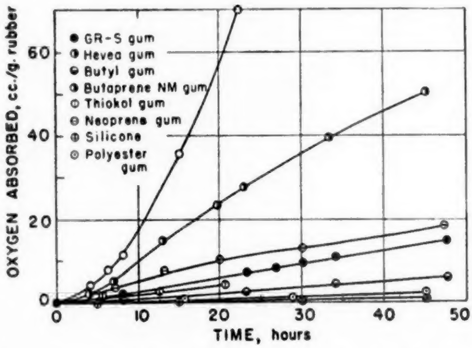


FIG. 14.—Absorption of oxygen by various rubber stocks at 130° C.

GR-S, Thiokol, Butyl, polyester, and silicone gum stocks, which are seen to absorb oxygen under these conditions in this order. There is a wide variation of oxygen absorption rate in passing from natural Hevea rubber to silicone rubber. In all cases, the greatest amount of oxygen was absorbed in a given time interval by those polymers containing a double bond in the skeleton structure. The nature of the side groups in the various polymers also played a predominant role. Thus, it is observed that natural rubber containing a methyl side group on the carbon atom adjacent to the double bond picks up more oxygen than any of the other polymers studied which contain such side groups as chloride, cyanide, phenyl, and carbonyl. The conclusion that may be drawn, then, is that the presence of a double bond in the skeletal structure of a polymer and of a methyl side group both enhance the rate of absorption of oxygen, the double bond being more important. It is to be noted that both double bonds and methyl side groups may act as electron donors. When the methyl side group is replaced, however, by electrophilic side groups—such as chloride, cyanide, phenyl, or carbonyl—there is a retardation in the rate of oxygen absorption. Further experiments were carried out on other polymers including polyethylene, polyisobutylene (Vistanex), Lactoprene (copolymer containing 95 parts of ethyl acrylate and 5 parts of chlorovinyl ether), and rubber hydrochloride (see Figure 15). It is interesting to compare the rates of oxygen absorption of

polyisobutylene and polyethylene. Both have the same basic hydrocarbon structure (—C—C—C—C—) but, since polyisobutylene contains two methyl side groups on every other carbon atom (as would be expected), it absorbs oxygen more rapidly than does polyethylene. Both of these stocks showed brief inhibition periods—the longest being that of polyethylene. By comparing the polyisobutylene stock with natural rubber it may also be shown that the double bond is more predominant than the side groups in determining the rate of oxygen absorption. Natural rubber has the basic structure [—C—C(CH_3)=

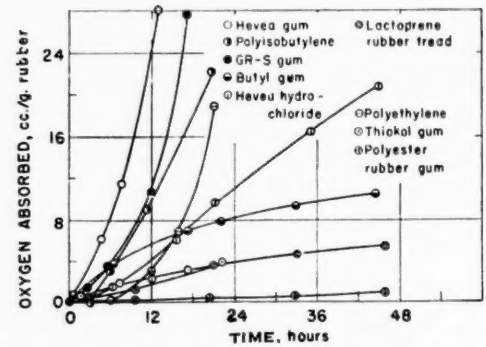


FIG. 15.—Absorption of oxygen by various polymers at 130° C.

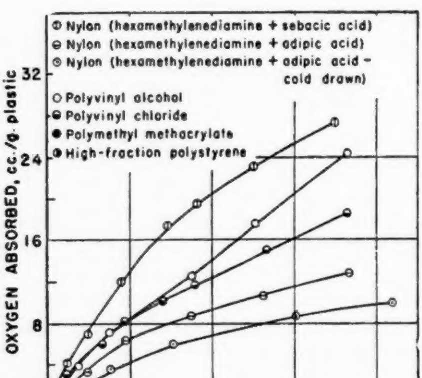


FIG. 16.—Absorption of oxygen by various plastics at 130° C.

C—C—], which contains a double bond and a methyl side group, while polyisobutylene has no double bonds but contains two methyl side groups. As can be seen from Figure 15, natural rubber absorbs oxygen most rapidly. However, when the double bonds in natural rubber have been saturated by treatment with hydrogen chloride to form rubber hydrochloride, there is an extreme retardation in the rate of oxygen absorption, to the extent that the rubber hydrochloride absorbs far less oxygen than polyisobutylene.

Studies of oxygen absorption have also been carried out on various other

types of plastics, as shown in Figure 16. It was observed that both polystyrene and polymethyl methacrylate absorbed very little oxygen, whereas the two plastics, polyvinyl alcohol and polyvinyl chloride, absorbed at least a tenfold larger amount. There appears to be a rough correlation between the ease of polymerization and the amount of oxidizability of a given plastic. Thus monomethyl methacrylate polymerizes rapidly to a polymer which absorbs oxygen very slowly at elevated temperatures. Vinyl chloride, on the other hand, polymerizes more slowly and with greater difficulty, and its rate of oxygen absorption is rapid compared to the methacrylate polymer. Comparisons are also shown (in Figure 16) between two different types of nylon plastics. One was prepared by condensation of hexamethylenediamine with adipic acid [$HOOC(CH_2)_4COOH$], the other by condensation with sebacic acid [$HOOC(CH_2)_8COOH$]. It is quite obvious that Nylon prepared from sebacic acid contains fewer amide groups per given number of carbon atoms in each repeating unit than Nylon prepared from adipic acid. Since the amido groups behave in a fashion similar to the behavior of the chloride, cyanide, and phenyl groups, *i.e.*, retard the rate of oxygen absorption, it would be expected that Nylon prepared from sebacic acid would absorb oxygen faster than Nylon prepared from adipic acid. This was actually observed, as shown in Figure 16. A further small retardation in the rate of oxygen absorption was also observed when Nylon prepared from adipic acid was cold-drawn about three times its original length to align the polar groups in the molecule. This is most probably a diffusion effect.

EFFECT OF ANTIOXIDANTS ON RATE OF OXYGEN ABSORPTION

We may summarize by saying that polyethylene acts as a base line of oxidizability. The presence of methyl side groups or double bonds along the chain greatly enhances oxidizability, whereas electrophilic side groups retard oxidizability. This is to be compared with the fact that alkyl-substituted ethylenes and allenes polymerize slowly, giving low molecular-weight polymers; ethylene itself polymerizes with some difficulty, and the introduction of a negative side group in ethylene gives compounds which polymerize rapidly to high molecular-weight materials (see Table I, in which allene is compared with polybutadiene because we are discussing the activity of the γ-carbon atom).

These conclusions are valid only for heat aging in the absence of light. They are limited by the fact that certain unknown impurities in the samples that we studied may have greatly enhanced or retarded the rate of oxygen absorption.

It has been observed for some time that various types of chemical agents are effective in retarding the extent of heat-deterioration of rubber polymers. In Figure 17, for example, is shown the effect of two chemical agents, benzoyl peroxide and P.B.N.A., on the rates of continuous and intermittent stress relaxation of GR-S gum stock. The benzoyl peroxide appears to have a deleterious effect in that the rate of continuous stress relaxation is faster than in either the control rubber containing no chemical agent or the gum stock containing P.B.N.A. Also, the rate of stress increase (indicating a hardening effect), as measured by intermittent stress relaxation, is most rapid for the rubber containing benzoyl peroxide and slowest for the stock containing P.B.N.A., thereby showing that both cross-linking and scission are accelerated by benzoyl peroxide and retarded by P.B.N.A. Oxygen absorption studies

TABLE I

COMPARISON OF OXIDIZABILITY OF POLYMERS WITH POLYMERIZATION OF MONOMERS

Polymerization		Oxidizability	
H C=C ‖ H HC H	Allene	H H C—C— ‖ H HC |	Polybutadiene (carbon-carbon double bonds along chain)
H H C=CH | H_3C	Propylene	H H —C—C— | H H_3C	Methyl side groups
Polymerize with difficulty		*Oxidize easily*	
H H HC=CH	Ethylene	H H —C—C— H H	Polyethylene
H H C=C | H H_5C_6	Styrene	H H —C—C— | H H_5C_6	
H H C=C X H	Vinyl compound (negative side group)	H H —C—C— X H	
Polymerize easily		*Difficult to oxidize*	

have also been made on similar rubber samples, as shown in Figure 18. It may be observed from this graph that the initial rate of oxygen absorption is greatest in the stock containing benzoyl peroxide and slowest in the stock containing P.B.N.A. The pronounced deleterious effect of benzoyl peroxide on physical properties and its effect on increased oxygen absorption rate may perhaps be attributed to its ability to initiate radical chains and hydroperoxide groups on the rubber molecule. The retardation of the rate of oxygen absorption occurring after a fairly long time interval is believed to be due to a retardation of diffusion caused by the formation of an extremely hard surface skin. In a recent article, Le Bras[21] has proposed two modes of action of antioxidants in rubber. There are substances of the first type which inhibit the combination of oxygen with rubber by preferential reactivity of oxygen with themselves. Substances of the second type are proposed which do not retard the reaction

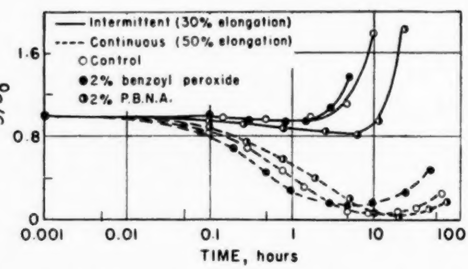


FIG. 17.—Effect of chemical agents on stress relaxation of GR-S at 130° C.

of oxygen with rubber but serve the purpose of deactivating the hydroperoxides formed on the rubber. The second type of antioxidants is more effective in preserving the physical properties of an aged rubber sample than antioxidants of the first type. Best results were obtained, however, by using combinations of two different types of antioxidants.

Figure 19 shows the effect of varying antioxidant concentration on the rate of oxygen absorption of GR-S gum stock. It is seen that the addition of 0.5 per

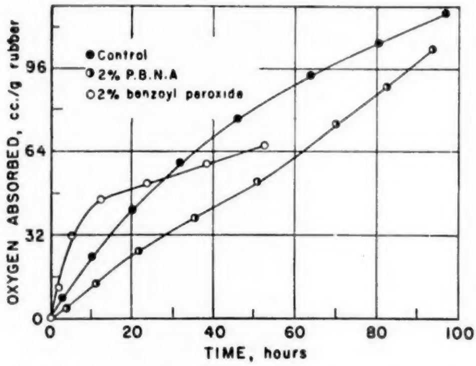


FIG. 18.—Effect of chemical agents on oxygen absorption of GR-S at 130° C.

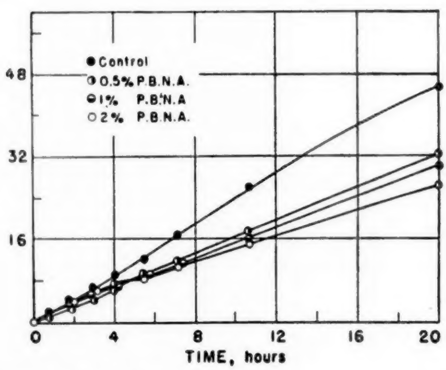


FIG. 19.—Effect of chemical agents on oxygen absorption of GR-S at 130° C.

cent of P.B.N.A. effectively retards the rate of oxygen absorption, as compared to the control, and that successively larger amounts of antioxidant (1.0 and 2.0 per cent) are even more effective during the later stages of oxidation.

EFFECT OF COMPOUNDING AND VULCANIZATION ON RATE OF OXYGEN ABSORPTION

The results on studies of the influence of vulcanization on the oxidizability of rubber are to be found extensively in the literature. It has been shown by Dufraisse and Le Bras[22], for example, that the rate of oxidation of rubber increases with higher proportions of combined sulfur. There is an upper limiting concentration of sulfur, however, at which the rate of oxidation remains

essentially constant. At very low concentrations of sulfur, a lower limit of oxidizability was observed, at which the rate of oxidation passed through a minimum. Dufraisse and Le Bras also studied the effect of sulfurless curing, using such agents as litharge and dinitrobenzene. They observed a retarded rate of oxidation in rubber stocks that were sulfurless-cured, compared to sulfur-cured stocks.

In Figure 20 the results found on oxygen absorption of Hevea rubber prepared under varying conditions are shown. The cast latex sheet absorbed a slightly larger amount of oxygen than the tread stock, although the rate for the cast latex sheet was initially slower, due to an induction period of several hours.

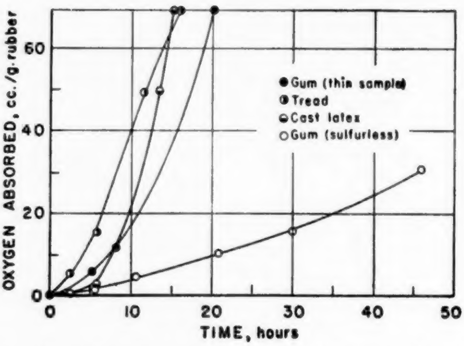


FIG. 20.—Absorption of oxygen by vulcanized Hevea stocks at 130° C.

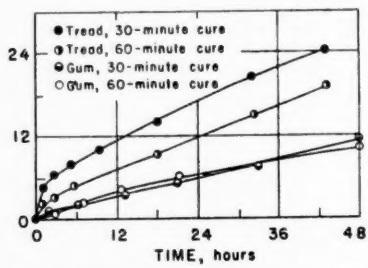


FIG. 21.—Effect of curing time on oxygen absorption of GR-S gum and tread stocks at 130° C.

The sulfurless Hevea gum stock showed at least a sevenfold retardation in oxygen absorption rate, compared to a similar sulfur-cured gum stock. It is evident that rubber stocks containing compounded sulfur tend to oxidize more readily. Also shown in Figure 20 are the results found on oxygen absorption of Hevea tread stocks. It is interesting to note that the tread stock absorbs more oxygen in a given time interval than the corresponding gum stock. In physical aging tests, such as continuous and intermittent stress relaxation experiments, it was observed that there was very little difference between the aging of gum and tread stocks of a given polymer. The discrepancy observed between gum and tread stocks in measurements of oxygen absorption rate may be due in part to partial absorption of oxygen on the available surface of the carbon black in the tread stocks. Free carbon black of large surface area will show a pronounced oxygen uptake in our oxygen absorption apparatus at 130° C.

Figure 21 shows the results of oxygen absorption experiments on GR-S gum and tread stocks cured for two different lengths of time. There appears to be a dependence of the oxidizability of this polymer both on curing time and compounding[23]. The two tread stocks cured for 30 and 60 minutes absorbed oxygen at a much faster rate than the two corresponding gum stocks also cured for

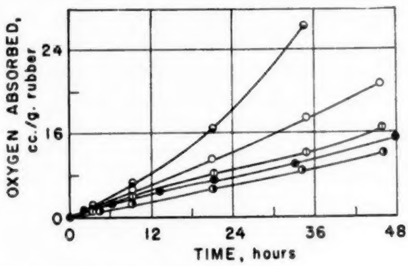


FIG. 22.—Absorption of oxygen by various copolymer gum stocks at 130° C; 30-minute cure.

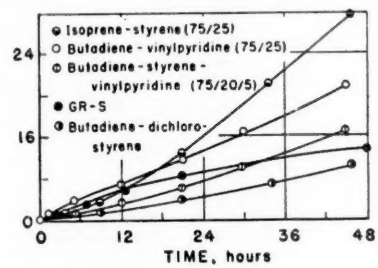


FIG. 23.—Absorption of oxygen by various copolymer gum stocks at 130° C; 60-minute cure.

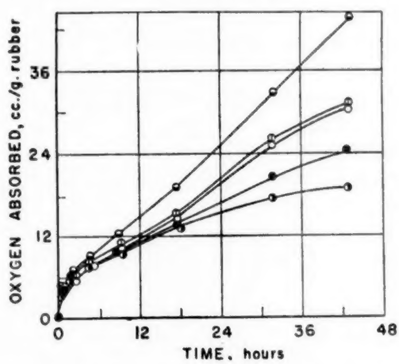


FIG. 24.—Absorption of oxygen by various copolymer tread stocks at 130° C; 30-minute cure.

30 and 60 minutes. There was also a large difference in absorption rate between the two tread stocks of different cures. This difference was not so pronounced with the gum stocks, although in the cases of both gum and tread stocks the polymer cured for 60 minutes was more stable toward oxidation than the corresponding polymer cured for 30 minutes. Further experiments of this kind were carried out on different types of copolymers (Figures 22–25) and

similar results were obtained in all cases. The various copolymer types studied were isoprene-styrene (75/25), butadiene-vinylpyridine (75/25), butadiene-styrene-vinylpyridine (75/20/5), butadiene-styrene (75/25), and butadiene-dichlorostyrene (75/25)—listed in the order of decreasing oxidizability for the gum stocks. With the tread stocks, the sequence of the butadiene-vinylpyridine and the butadiene-styrene-vinylpyridine was interchanged. Studies of continuous stress relaxation were previously performed on these polymers, and it was observed that the rate of stress relaxation was in the same order as listed for the rate of oxygen absorption. Furthermore, a similar interchangeability was noted between gum and tread stocks of the butadiene-vinylpyridine and butadiene-styrene-vinylpyridine polymers.

It is interesting also to note with regard to these different copolymers (Figures 22–25) that their rates of oxidation were in complete accordance with the expected rates, when considered on the basis of their chemical structure.

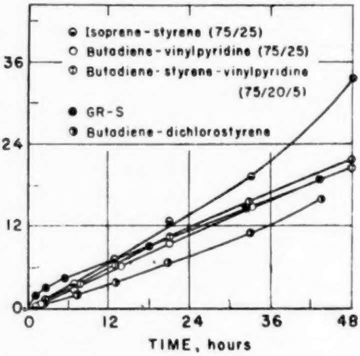


FIG. 25.—Absorption of oxygen by various copolymer tread stocks at 130° C; 60-minute cure.

The oxygen absorption data presented up to now have been confined exclusively to a static system. Under such conditions the rate of uptake of oxygen by the polymer at constant temperature and pressure is measured as a function of time. Any evolution of gaseous oxidative products during the course of the experiment would tend to decrease the observed amount of oxygen absorbed, compared to the actual amount of oxygen absorbed. Through the use of a circulating, rather than a static, system it is possible to trap the gaseous oxidative products evolved and thus measure the true oxidizability of polymers. The most common gaseous oxidative products believed to be evolved are carbon dioxide, carbon monoxide, water vapor—and in some special cases, formaldehyde and other aldehydes, and organic acids. By passing these gases through a column of Ascarite (sodium hydroxide and calcium oxide suspended on asbestos) and Hopcalite (specially prepared manganese dioxide containing small amounts of copper oxide), they are successfully removed from the system and contribute almost a negligible vapor pressure.

To determine whether the evolution of gaseous oxidative products had any effect on the relative rates of oxidizability of the various rubbers and plastics previously studied, a circulating oxygen absorption apparatus was built.

A diagram of the circulating system used is shown in Figure 26. The pressure control is made by raising the level of mercury in the reservoir, R_1, to a height at which the contact between the meniscus of the mercury in the

manometer and the tungsten electrode, E_1, is just broken. As the oxygen is absorbed, the pressure decreases and the mercury makes contact with E_1. This closes an electric circuit which sends current through the electrolytic cell. The gas generated exerts a pressure on the surface of the mercury reservoir, R_2, forcing the mercury into the gas buret. This builds up the pressure inside, which results in breaking the contact between E_1 and the meniscus. Constant temperature is attained by placing the Pyrex glass tubing containing the polymeric sample in the vapor of a boiling liquid. (In the case of the data to be discussed in this paper, a constant temperature of 131° C was attained by refluxing chlorobenzene.)

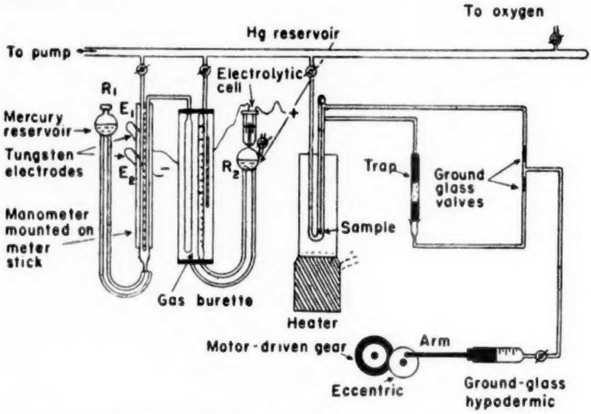


FIG. 26.—Circulating system for measuring oxygen absorption.

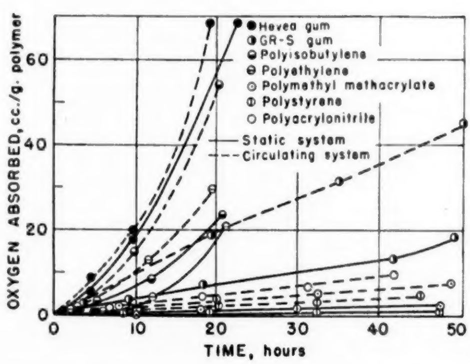


FIG. 27.—Comparison of absorption of oxygen by various polymers using the static and circulating systems at 130° C.

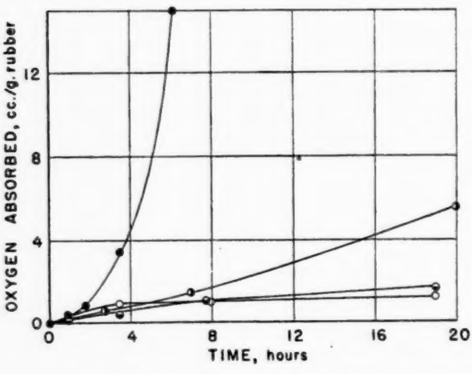
Circulation of the oxygen and gaseous products evolved in the system was carried out in the following manner. An electric motor-driven gear was arranged to rotate the eccentric at a constant rate. An arm was attached to the eccentric, which moved in a pistonlike stroke eight times per minute. The movement of the arm operated the plunger of the ground glass hypodermic. During the compression stroke of the plunger the upper ground glass valve opened and the lower ground glass valve was forced shut. On the expansion

stroke of the plunger the upper valve remained shut and the lower valve opened. A circulation of the gas in the system was thus maintained through the trap of Hopcalite and Ascarite shown in the diagram of the apparatus.

To compare the amounts of oxygen absorption in various polymers between the static and circulating systems, a run was carried out at 130° C. Figure 27 shows the oxygen absorption of Hevea, polyisobutylene, polyethylene, GR-S, polyacrylonitrile, polymethyl methacrylate, and polystyrene, which are seen to absorb oxygen in this order. The order given above is the same whether the studies were made with the circulating or the static system. However, it can be seen from the data that the amount of oxygen absorbed for any one of the polymers mentioned above is always somewhat greater when measured by the circulating, than by the static system. This result indicates clearly that gaseous oxidative products are given off which should be accounted for when studying the relative rates of oxidizability of various polymers.

EFFECT OF LIGHT ON AGING OF RUBBER AS MEASURED BY OXYGEN ABSORPTION AND STRESS RELAXATION

Throughout this paper we have emphasized the importance of a radical mechanism for the degradation of vinyl and diene polymers in which oxygen



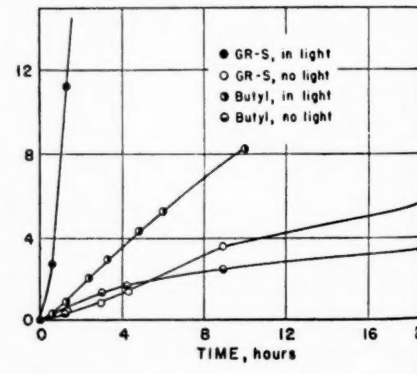


FIG. 28.—Absorption of oxygen by GR-S and Butyl in presence and absence of light at 100° C.
FIG. 29.—Absorption of oxygen by GR-S and Butyl in presence and absence of light at 70° C.

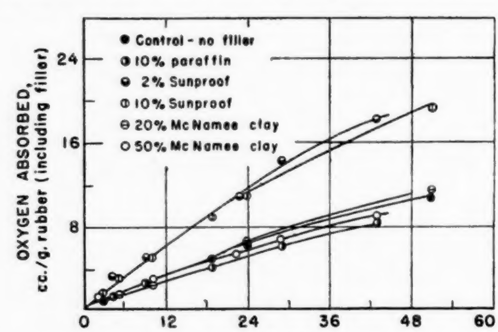


FIG. 30.—Absorption of oxygen by Butyl rubber compounded with various fillers at 55° C.

plays a predominant role. It is to be expected on the basis of a radical mechanism that the presence of light in the wave length region of 2800–3000 Å., acting as a chain initiator, should greatly accelerate the aging process. From preliminary studies of oxygen absorption and stress relaxation in the presence of light on translucent gum stocks of Butyl and GR-S rubbers, there is little doubt that light has a pronounced effect on all the aging processes[24].

Samples of pure-gum vulcanizates of GR-S and Butyl were aged at 70° and 100° C in the presence and absence of light from an RS sun lamp (17 inches from the samples). The resulting oxygen absorption curves at these temperatures are shown in Figures 28, 29, and 30, in which the cubic centimeters of oxygen absorbed per gram of rubber is plotted against the exposure time (in hours). The studies were made in a static system. Four conclusions may be readily drawn from these curves: (1) GR-S absorbs oxygen faster than does Butyl, as has been explained previously; (2) light increases the rate of absorption—and much more so for GR-S than for Butyl; (3) heat increases the rate of oxygen absorption; and (4) the increased rate of absorption due to light is greater at higher temperatures[25].

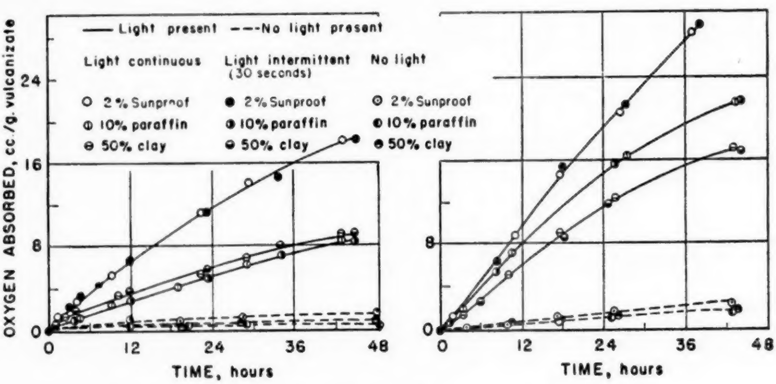


FIG. 31.—Absorption of oxygen by Butyl translucent stock at 55° C; the light source was 17 inches away.
FIG. 32.—Absorption of oxygen by Butyl translucent stock at 95° C; light source was 17 inches away.

Samples of Butyl rubber films containing various fillers and waxes were exposed to the light of a General Electric RS lamp at 55° C in an oxygen atmosphere; the light was 17 inches away. In Figure 30 the cubic centimeters of oxygen absorbed per gram of vulcanizate (including filler) is plotted against exposure time. The control film was the same as the Butyl films used in the previous experiments. Samples containing 10 per cent paraffin, 2 and 10 per cent Sun-proof, and 20 and 50 per cent McNamee clay were used. The rubbers containing the paraffin and the clays absorbed oxygen at the same rate as the base formation rubber; the rubbers containing Sun-proof absorbed oxygen at a faster rate. Whereas waxes offer protection against ozone attack in unsaturated rubbers, *i.e.*, Hevea or GR-S, they do not necessarily retard photoactivated oxidation. The clay filler also appeared to have an accelerating effect on photoactivated oxidation.

A very interesting experiment was performed by subjecting samples aging at 55° and 95° C in an oxygen atmosphere to an intermittent light source.

The samples were exposed to the light for 30-second intervals—30 seconds in the presence of light and 30 seconds in the absence of light. Thus in 20 hours the samples were exposed to light for 10 hours. Runs were also made at the same temperatures with no light present. The results are shown in Figures 31 and 32. It is evident that the rate of absorption was the same for the samples exposed to light, whether intermittently or not, and was much greater in these cases than for the samples exposed in the dark. This indicates that the absorption continues during the 30-second interval of darkness of the intermittent light experiment. Experiments employing different periods of intermittent lighting would be of great interest from the point of view of elucidating the mechanism of oxygen absorption.

Previously in this paper it was stated that continuous stress relaxation studies provide a method of isolating the scission reaction whereas intermittent stress relaxation measures the sum of cross-linking and scission. To study the effect of light on the reactions of scission and cross-linking, relaxation studies at 50 per cent elongation were made on the samples of thin (0.004 inch) translucent Butyl films in the presence and absence of light over a wide temperature range. The source of light used was an RS sun lamp. The door of the stress relaxation box was fitted with a thin sheet of cellophane to keep the heat in the box and yet allow light to pass through to the sample.

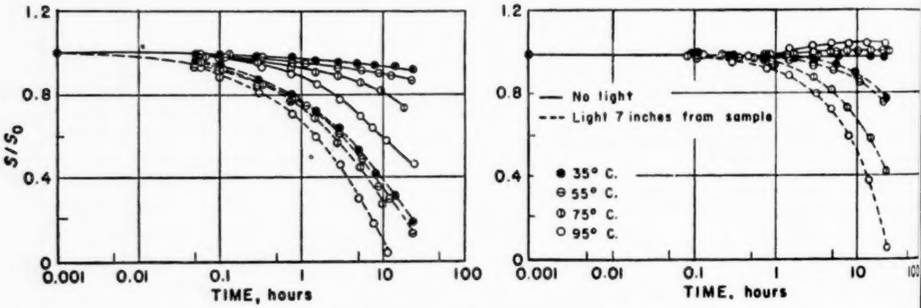


FIG. 33.—Continuous stress relaxation of Butyl translucent stock; 50% elongation.
FIG. 34.—Intermittent stress relaxation of Butyl translucent stock; 50% elongation.

In Figure 33 data are shown on the rate of continuous stress relaxation, both in the absence of light and when the light was placed 7 inches from the rubber samples for temperatures of 35°, 55°, 75°, and 95° C. In these graphs stress divided by initial stress is plotted against logarithmic time. It is evident that light had an important accelerating effect on the rate of stress relaxation.

Studies of intermittent stress relaxation in light and in darkness were also performed at the same four temperatures (Figure 34). There was no appreciable change in modulus of the stock during the course of the experiments performed in the absence of light. In the presence of light there was a rapid decrease in the intermittently measured stress, *i.e.*, a softening of the stocks, which became more rapid with increasing temperature. From these stress relaxation studies on Butyl rubber it becomes evident that light accelerates the aging process and especially the disaggregative reaction leading to scission.

The mechanism of photoöxidation probably involves the same elementary reactions as were postulated for heat oxidation, except that light may initiate radical chains and thus accelerate the entire process.

SUMMARY

The chemical reactivity of vinyl and diene polymers manifested during aging and degradation is similar to the reactivity manifested during polymerization. The activated intermediates are radicals, and the reaction proceeds by a chain mechanism. A discussion of the possible types of aggregative and disaggregative processes involved in aging is presented. On the basis that polymerization and degradation occur by means of the same radical mechanism, experimental evidence is given to indicate that under certain conditions both reactions may occur simultaneously. Viscosity changes of solutions of mono- and polystyrene and methyl methacrylate were studied under varying conditions of heat, oxygen, catalysts, light, and photosensitizers. An analysis of the concurrent aggregative and disaggregative reactions involved in aging may be obtained by isolating one reaction from the other, either by various physical methods, such as intermittent and continuous stress relaxation, or by such classical methods as sol–gel determinations and aging in solution. A comparative study of the rate of oxygen absorption of a large number of polymer types was undertaken to evaluate the factors affecting oxidation. Evidence is presented to show that these factors may be specified by the following: (1) chemical structure of the polymeric material, (2) presence of antioxidants, and (3) compounding and vulcanization. The oxidizability of polymeric materials was also studied in a circulating oxygen absorption apparatus to determine the effect of evolved, gaseous oxidation products. A preliminary study of the effect of light on the aging of Butyl and GR-S, measured by oxygen absorption and stress relaxation, is presented.

ACKNOWLEDGMENT

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REFERENCES

[1] Spence and Ferry, *J. Am. Chem. Soc.* **59**, 1648 (1937).
[2] Staudinger, *Proc. Rubber Tech. Conf. London*, **1938**, p. 253.
[3] Schulz, *Z. physik. Chem.* **43B**, 25 (1939).
[4] Stevens, *J. Soc. Chem. Ind.* **64**, 135 (1945).
[5] Taylor and Tobolsky, *J. Am. Chem. Soc.* **67**, 2063 (1945).
[6] Chalmers, *J. Am. Chem. Soc.* **56**, 912 (1934).
[7] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, p. 125.
[8] George and Walsh, *Trans. Faraday Soc.* **42**, 94 (1946).
[9] Medvedev and Zeitlin, *Acta Physicochim.* **20**, 3 (1945).
[10] Barnes, *J. Am. Chem. Soc.* **67**, 217 (1945).
[11] Kolthoff and Dale, *J. Am. Chem. Soc.* **67**, 1672 (1945); Price and Adams, *J. Am. Chem. Soc.* **67**, 1674 (1945).
[12] Staudinger, *Ber.* **58**, 1075 (1925).
[13] Stevens, RUBBER CHEM. TECH. **18**, 610 (1945).
[14] Mayo and Lewis, *J. Am. Chem. Soc.* **66**, 1594 (1944).
[15] Alfrey and Goldfinger, *J. Chem. Physics* **12**, 205 (1944).
[16] Mayo, *J. Am. Chem. Soc.* **65**, 2324 (1934).
[17] Mesrobian and Tobolsky, *J. Am. Chem. Soc.* **67**, 785 (1945).
[18] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).
[19] Andrews, Tobolsky, and Hansen, *J. Applied Physics* **17**, 352 (1946).
[20] Bolland and Gee, *Trans. Faraday Soc.* **42**, 236 (1946).
[21] Le Bras, RUBBER CHEM. TECH. **18**, 22 (1945).
[22] Dufraisse and Le Bras, *Proc. Rubber Tech. Conf. London*, **1938**, p. 555.
[23] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946).
[24] These stocks were prepared by Murray Jelling at the Polytechnic Institute of Brooklyn.
[25] Jelling, Mesrobian, and Tobolsky, "Report on Coated Fabrics and Thin Films", Quartermaster Corps Project, Inst. of Polymer Research, Polytechnic Institute of Brooklyn, Oct. **1943**–Jan. **1946**, p. 200.

COPOLYMERS OF BUTADIENE WITH HALOGENATED STYRENES *

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In seeking new copolymers of butadiene which might show rubberlike properties superior to those of the styrene copolymer, the authors were led by numerous reports on chlorostyrene derivatives[1] to make a study of halogenated styrenes. The chlorostyrenes are potentially available in quantity and should be reasonably cheap. The present work was undertaken to obtain fundamental information on the copolymerization of these halogenated styrenes with butadiene as well as to learn what relative advantages and disadvantages the various copolymers would have as substitutes for rubber. In addition to various halogenated styrenes, the copolymerization of *p*-cyanostyrene and some derivatives is included in this report.

The methods of preparation of the new halogenated styrenes have been reported elsewhere[2]. The known compounds were made by the standard methods. The mixed mono-, di-, tri-, and tetrachlorostyrenes were furnished by the electrochemical Department of E. I. du Pont de Nemours & Company, Inc. The 2,5-dichlorostyrene was furnished by the Monsanto Chemical Company.

POLYMERIZATION

Most of the monomers were charged at a 25:75 weight ratio with butadiene in a typical emulsion polymerization recipe and polymerized as nearly as possible to 77 per cent conversion. A few of the more promising styrenes were also tested at a 15:85 ratio and at a ratio of x:75, where x is the molar equivalent of 25 parts of styrene. Halogen analysis showed to what extent the styrene had entered the copolymer.

Table I shows that some of the monohalogenated styrene copolymerizations went at a slightly slower rate than did the control. Thus *o*- and *p*-chlorostyrene, *m*- and *p*-fluorostyrene, and *m*-bromostyrene gave a slower overall rate; on the other hand, *m*-chlorostyrene, the mixed chlorostyrenes, and *o*- and *p*-bromostyrene gave a normal conversion in 11 hours. It is possible that traces of inhibiting impurities in the monomers were responsible for some of these anomalous results. Among the dichlorostyrenes the 2,3-, 2,4-, and mixed isomers had a normal rate; the 2,6-isomer slowed the polymerization considerably; and the 2,5- and 3,4-isomers (on the basis of data not shown) copolymerized somewhat more rapidly than styrene. The tri- and tetrachlorostyrenes gave progressively slower polymerization rates. Very little pentachlorostyrene appeared in the copolymer. *p*-Cyanostyrene copolymerized normally.

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TABLE I

EMULSION COPOLYMERIZATION OF BUTADIENE AND HALOGENATED STYRENES AT 50° C

Comonomer	Weight ratio, butadiene: styrene	Time (hr.)	Conversion (%)	Benzene solubility (%)	[η]	Halogenated styrene (%)
Styrene	75:25	11	77	98	2.12	—
o-Chlorostyrene	75:25	11	66	96	2.09	23.3
	75:33.5	19	74	100	2.06	29.7
	85:15	14½	72	92	1.89	14.2
m-Chlorostyrene	75:25	11	78	94	1.82	25.0
p-Chlorostyrene	75:33.7	12	67	100	1.64	26.7
Mixed chlorostyrenes	75:25	11½	77	95	1.55	25.8
α-Chlorostyrene	75:25	36	0	—	—	—
2,3-Dichlorostyrene	75:25	11½	75	94	1.16	27.5
2,4-Dichlorostyrene	75:25	12	76	95	1.65	23.0
2,5-Dichlorostyrene*	75:25	11	80	99	1.52	28.2
	75:41.6	12	89	99	2.05	38.1
2,6-Dichlorostyrene	75:25	16	72	90	1.92	14.3
3,4-Dichlorostyrene*	75:25	12	80	93	1.78	27.3
	75:41.6	12	81	100	1.89	36.2
	85:15	12	77	94	2.06	16.4
3,5-Dichlorostyrene	75:25	9½	75	99	1.24	27.1
Mixed dichlorostyrenes	75:25	11¾	75	96	1.52	26.2
Mixed trichlorostyrenes	75:25	14½	71	93	1.60	20.0
Mixed tetrachlorostyrenes	75:25	37	80	46	1.13	24.1
Pentrachlorostyrene*	75:25	12	65	100	Low	3.9
m-Fluorostyrene	75:25	12	70	96	1.44	24.3
p-Fluorostyrene	75:25	14	71	96	2.01	†
o-Bromostyrene	75:25	11½	79	99	1.63	26.8
m-Bromostyrene	75:25	13	75	92	1.55	26.6
p-Bromostyrene	75:25	10	74	92	1.19	23.4
p-Cyanostyrene	75:25	10½	72	97	1.34	26.1
p-Carboxystyrene*	75:25	22	41	13	0.44	†
p-Carboxystyrene (Na salt)*	75:25	20	100	12	0.47	†
p-Carbomethoxystyrene*	81:19	15	59	100	1.33	†

* Not evaluated.
† Not analyzed.

α-Chlorostyrene caused the emulsion to break, perhaps because the halogen alpha to the ring was no longer protected by its position on an olefinic carbon atom once polymerization had begun, so it was hydrolyzed to give hydrochloric acid; in any event, breaking of the emulsion prevented any appreciable polymer formation.

The ratio at which the two monomers enter a copolymer is significant in relation to the properties of the product, for it determines whether there is homogeneity of structure from one molecule to the next. Wall[3] has defined the value α as the exponent in the equation:

$$\frac{n_x}{n_x^0} = \left(\frac{n_y}{n_y^0}\right)^\alpha$$

where n_x and n_y are the number of unpolymerized molecules of two monomers, x and y, after a given time of polymerization has elapsed, when n_x and n_y molecules of the two monomers were present at the beginning of the reaction. Wall points out that only in an ideal copolymerization, where α is unity, do the monomers enter the polymer in the ratio at which they are charged, but that for monomer pairs having α values between ½ and 2 the homogeneity of mono-

mer distribution throughout the polymer chains is reasonably great. Table I shows the fractions of the halogenated styrenes found in the copolymers by halogen analysis (except for the fluoro- and cyanostyrenes, which were analyzed by other means); from these fractions the α values have been calculated (Table II). Only those for 2,6-dichlorostyrene and pentachlorostyrene with butadiene

Table II

Values of α for Emulsion Copolymerization of Butadiene and Halogenated Styrenes, 50° C, as Found at 75:25 Charging Ratio and Conversions Shown in Table I

Substituted styrene	α
Styrene[4]	0.61
o-Chlorostyrene	0.86
m-Chlorostyrene	1.0
Mixed monochlorostyrenes	1.1
2,3-Dichlorostyrene	1.3
2,4-Dichlorostyrene	0.80
2,5-Dichlorostyrene	1.6
2,6-Dichlorostyrene	0.31
3,4-Dichlorostyrene	1.4
3,5-Dichlorostyrene	1.3
Mixed dichlorostyrenes	1.2
Mixed trichlorostyrenes	0.59
Mixed tetrachlorostyrenes	0.89
Pentachlorostyrene	Very low
m-Fluorostyrene	0.93
o-Bromostyrene	1.3
m-Bromostyrene	1.2
p-Bromostyrene	0.84
p-Cyanostyrene	1.1

do not fall within the limits proposed. The symbol y has been assigned to butadiene in these calculations, so that a value of α greater than unity indicates that the substituted styrene enters the polymer faster than does the butadiene.

It is evident that there is no correlation between the overall polymerization rate and the rate at which the comonomer enters, except that both 2,6-dichlorostyrene and pentachlorostyrene have abnormally low rates and low α values. Of the styrenes examined, *o*- and *m*-bromo- and all the dichlorostyrenes except the 2,4- and 2,6-isomers enter the copolymer most rapidly, in all cases faster than the butadiene. With the dichlorostyrenes the quality of the rubber seems to be directly related to the relative rate of entry, for the 2,5- and 3,4-isomers give the best copolymers and the 2,4- and 2,6-isomers the poorest.

Monomers.—The mixed mono-, di-, tri-, and tetrachlorostyrenes were furnished by the Electrochemical Department of E. I. du Pont de Nemours & Company, Inc. The following data accompanied these samples:

Monochlorostyrenes	
Chlorostyrene content (Br_2 titration) (%)	97.5
d_4^{15}	1.099
n_D^{25}	1.5638
B.p. around 2 mm. (° C)	38.0–42.0
Dichlorostyrenes	
d_4^{15}	1.285
n_D^{20}	1.5812
B.p. at 2 mm. (° C)	67–70
Stabilizers	*p-tert*-amylphenol and diphenylamine, 0.1% each

Trichlorostyrenes	
Trichlorostyrene content (Br_2 titration) (%)	88
d_4^{15}	1.408
n_D^{20}	1.5951
B.p. at 2 mm. (° C)	105–110
Stabilizer	Hydroquinone
Tetrachlorostyrene	
d_4^{15}	1.509
n_D^{20}	1.6066
B.p. at 3 mm. (° C)	126–129
Stabilizers	*p-tert*-amylphenol and diphenylamine, 0.1% each

The mono- and trichlorostyrenes were used as received. The di- and tetrachlorostyrenes were washed with 5 per cent sodium hydroxide and water, dried, and distilled at reduced pressure in a nitrogen atmosphere.

2,5-Dichlorostyrene was furnished by the Monsanto Chemical Company. It was washed and dried before use. The methods of preparation of the monohalostyrenes have been reported by Brooks[5] and Marvel and coworkers[6]. The transformation of styrene to α-chlorostyrene was made according to the directions of Bilz[7] and of Emerson and Agnew[8]. Pentachlorostyrene was prepared from ethylbenzene by methods found in the patent literature[9]. *p*-Cyano, *p*-carbomethoxy-, and *p*-carboxystyrenes have been described[10].

The physical constants of the styrenes used in this study are given in Table III.

TABLE III

PHYSICAL CONSTANTS OF THE HALOGENATED STYRENES

	B.p. (° C)	Pressure (mm.)	n_D^{20}
o-Chlorostyrene	67–9	3–3.5	1.5638
m-Chlorostyrene	60–1	3	1.5620
p-Chlorostyrene	65	6–7	1.5648
α-Chlorostyrene	75–6	17	1.5612
2,3-Dichlorostyrene	93–5	4–5	1.5834
2,4-Dichlorostyrene	81	6	1.5828
2,6-Dichlorostyrene	70–2	4–5	1.5754
3,4-Dichlorostyrene	84	4	1.5750
3,5-Dichlorostyrene	59	1	1.5745 (25°)
Pentachlorostyrene	140–2	0.5	1.5965
m-Fluorostyrene	30–2	2	1.5170
p-Fluorostyrene	57–9	13–14	1.5156
o-Bromostyrene	64–5	3	1.5914
m-Bromostyrene	74–5	3	1.5903
p-Bromostyrene	88	12	1.5950 (19°)
p-Cyanostyrene	102–4	9	1.5781

Butadiene was the special purity grade supplied by the Phillips Petroleum Company; it was passed over sodium hydroxide pellets and condensed in a dry-ice trap.

Polymerization.—The polymerizations were carried out in 4-ounce screw-cap bottles (or, in a few instances, in 28-ounce crown-cap bottles) whose caps were fitted with rubber disk gaskets lined with heavy tin foil. The charge for a 75:25 run was as follows in parts by weight:

Butadiene	75.0 parts
Substituted styrene	25.0
Soap (Proctor and Gamble silica-free flakes)	5.0
Water	180.0
Potassium persulfate	0.30
Dodecanethiol (pure)	0.35

The soap was dissolved in 170 parts of water and charged into the bottle with 10 parts of freshly prepared 3 per cent potassium persulfate solution. The substituted styrene, containing the proper proportion of dodecanethiol, was added, and the mixture was shaken and thoroughly chilled in ice water. Slightly more than 75 parts of butadiene was poured into the weighed bottle, and the excess was allowed to boil off to remove air before the cap was put in place. The bottles were rotated end over end for the specified time in a bath at 50° ± 1° C.

The cooled latex was mixed with 25 parts of a 10 per cent suspension of phenyl-β-naphthylamine in soap solution and coagulated with a saturated sodium chloride solution containing 2.3 per cent of concentrated sulfuric acid. The rubber was washed repeatedly with water, cut or broken into small pieces, and dried overnight at 70–80° C in a vacuum oven at 85 mm. In calculating conversion, the residual fat acid and antioxidant were taken into account. It was assumed, perhaps without justification, that the unpolymerized styrene would be removed by the vacuum drying.

Analysis.—Samples were prepared for halogen analysis by twice dissolving the polymer in benzene and precipitating it with methanol, then drying in the vacuum oven. Fluorostyrene content was determined by comparison of the ultraviolet absorption spectra of the copolymer and of pure polyfluorostyrene[11].

TABLE IV

ANALYSES* OF 75:25 COPOLYMERS

Comonomer	Halogen found (%)	Carbon (%)		Hydrogen (%)		Ash (%)	Total
		Calcd.†	Found	Calcd.†	Found		
o-Chlorostyrene	5.97	84.3	82.66	9.7	9.87	0.9	99.4
m-Chlorostyrene	6.40	84.0	83.73	9.6	9.71	—	99.8
2,3-Dichlorostyrene	11.3	79.8	79.33	9.1	9.36	—	100.0
2,4-Dichlorostyrene	9.44	81.2	81.16	9.4	9.35	—	100.0
2,5-Dichlorostyrene	11.58	79.4	79.61	9.0	8.90	—	100.1
2,6-Dichlorostyrene	5.85	84.1	83.38	10.0	10.04	—	99.3
3,4-Dichlorostyrene	11.2	79.6	77.90	9.0	9.10	—	98.2
3,5-Dichlorostyrene	11.1	79.8	77.94	9.0	8.65	—	97.7
o-Bromostyrene	11.7	79.2	79.25	9.1	9.23	—	100.2
m-Bromostyrene	11.6	79.3	79.58	9.2	9.42	—	100.6
p-Bromostyrene	10.2	80.4	78.52	9.4	9.08	—	97.8
p-Cyanostyrene	2.83‡	87.6	86.12	9.6	9.82	—	98.8

* These microanalyses were carried out by H. S. Clark of the Illinois State Geological Survey.
† Calculated from halogen content.
‡ Per cent nitrogen.

The carbon, hydrogen, and halogen analyses (Table IV) indicated that a few of the samples contained from 1 to 4 per cent of methanol; it is likely that an even larger residue of benzene remained, for benzene constituted three fourths of the purifying solvent, yet it would not affect the carbon-hydrogen ratio noticeably. It may be concluded that the true halogen contents, and consequently the proportions of halostyrenes, were higher than they appeared to be in these samples. This does not alter the fact that most of the substituted styrenes enter the copolymer more rapidly in relation to butadiene than does styrene.

Characterization of polymer.—The solubility of the material was normally determined by allowing a 0.4-gram sample, cut into small pieces, to stand 48 hours in 100 cc. of dry benzene in a closed bottle at room tempersture[12]. The liquid was decanted and filtered through a 100-mesh screen to remove gel; a

5-cc. aliquot was pipetted into a tared aluminum pan. When the solvent had evaporated, the pan was dried 2 hours in a circulating air oven at 70–80° C and weighed.

The gel-free solution was diluted with 2 parts of dry benzene, and its flow time was measured in an Ostwald viscometer at 25° C. From this value and the flow time for dry benzene the intrinsic viscosity, $[\eta]$, was computed by the following formula:

$$[\eta] = \frac{\ln t - \ln t_0}{c}$$

where t, t_0 = flow times of soln. and solvent
C = concn. of polymer (grams per 100 cc. soln.[12])

EVALUATION

The copolymers were evaluated in the following tread-type recipe, in parts by weight:

Copolymer	100.0
EPC carbon black	50.0
Zinc oxide	5.0
Stearic acid	1.5
Paraflux*	5.0
Santocure	1.2
Sulfur varied, when sample size permitted, to give optimum physical properties	

* A petroleum-type softener supplied by C. P. Hall Company.

The behavior of the rubber on the mill was noted in each case. Although the Mooney viscosity values varied widely, the mill behavior was in no case markedly different from that which would have been experienced with butadiene-styrene copolymers made to the same viscosity.

Stress-strain properties were determined by the Goodrich microtechnique[13]. Hysteresis temperature rise at 212° F was determined using the Goodrich flexometer[14] with a 55-pound load and a 17½ per cent stroke. Flexing results are reported in terms of the number of flexures required for an initiated crack to grow to an arbitrary rating of eight (about 75 per cent of a 1-inch width). A De Mattia machine was used, operating at 300 cycles per minute with a stroke of 2¼ inches in a room maintained at 82° F and 45 per cent relative humidity.

Quality index[15] is defined as the ratio of the observed flexures to the flexures of a similar GR-S tread stock having a hysteresis temperature rise equal to the observed hysteresis temperature rise. The relation between flexing and hysteresis temperature rise for a GR-S tread stock compounded with EPC black and for the particular test conditions used here is expressed by the following equation[15]:

$$\log_{10} \text{flexures} = 0.0126\Delta T + 4.28$$

where ΔT is the hysteresis temperature rise above 212° F, as determined by the Goodrich flexometer with a 55-pound load and a 17½ per cent stroke. The significance of the quality index has been discussed by Juve[15].

On the basis of the test results obtained (summarized in Table V) the following conclusions were reached:

1. In general, copolymers of the monohalogenated styrenes are equal in quality to GR-S. However, those of *o*-chlorostyrene, both 75–25 and 75–33.5,

TABLE V

EVALUATION OF COPOLYMERS

Comonomer	Ratio, butadiene: comonomer	Mooney viscosity*	Sulfur (parts)	Cure (min. at 280° F)	300% modulus (lbs. per sq. in.)	Tensile (lbs. per sq. in.)	Elongation (%)	Hysteresis temp. rise (° F)	Flexing†	Durometer hardness	Quality index[15]
No. 1 *o*-chlorostyrene	75:25	—	1.75	75	600	2750	685	105	1,280,000–8	—	3.3
				150	750	2600	640	70	730,000–8	—	5.1
GR-S control‡	—	—	1.75	75	550	2700	740	45§	350,000–8	—	—
				150	600	3150	750	42§	420,000–8	—	—
No. 2 *o*-chlorostyrene	75:33.5	51	1.75	75	1090	3880	607	109	880,000–8	74	1.9
				150	1200	4140	586	56	760,000–8	67	7.8
GR-S control	—	—	—	75	910	3050	607	—	310,000–8	59	—
				150	940	3170	575	47	200,000–8	65	2.6
No. 3 *o*-chlorostyrene	85:15	59	2.0	60	700	3140	710	—	—	—	—
				75	890	3320	665	—	385,000–8	64	—
				150	—	—	—	76	160,000–8	64	0.92
GR-S control	—	—	—	60	550	2790	790	—	—	—	—
				75	760	3490	713	97	286,000–8	57	0.86
				150	950	3140	633	62	190,000–8	60	1.6
No. 4 *m*-chlorostyrene	75:25	—	2.0	45	500	2700	860	—	—	—	—
				75	800	3300	760	—	2,000,000–3	—	—
				150	900	3800	720	122	2,000,000–6	—	3.0+
GR-S control	—	—	2.0	45	500	2700	825	—	—	—	—
				75	950	3500	745	63	480,000–8	—	4.0
				150	1100	3550	620	53	430,000–8	—	4.6
No. 5 *p*-chlorostyrene	75:33.7	—	—	30	600	2450	685	—	—	—	—
				45	950	2350	505	81	570,000–8	—	2.8
				75	1125	3000	550	—	—	—	—
GR-S control	—	—	2.0	45	400	2450	875	—	—	—	—
				75	600	3300	755	78	330,000–8	—	1.8
				150	950	3050	630	58	210,000–8	—	2.0

* Mooney value at end of 4-minute run using the large rotor at 212° F.

† Rating of crack length at the number of flexures shown. A rating of 1 means no crack and 10 is complete failure.

‡ With each experimental polymer or group of polymers a GR-S control was run. The values obtained for the control are shown in Table V along with those for the experimental polymer. Because of differences from time to time in the materials used and inadvertent differences in mixing, curing, and testing, conclusions as to the quality of the experimental polymers are based on its properties compared with the appropriate control.

§ This control showed exceptionally low hysteresis.

§ This control showed exceptionally low hysteresis.

TABLE V—*Continued*

Comonomer	Ratio, butadiene: comonomer	Mooney viscosity*	Sulfur (parts)	Cure (min. at 280° F)	300% modulus (lbs. per sq. in.)	Tensile (lbs. per sq. in.)	Elongation (%)	Hysteresis temp. rise (° F)	Flexing†	Durometer hardness	Quality index[15]
No. 6 mixed monochlorostyrenes	75:25	—	2.0	45	250	1850	1000	—	—	—	—
				75	650	3500	815	—	380,000–8	—	—
				150	1000	3500	670	44	230,000–8	—	3.3
GR-S control	—	—	2.0	45	200	1550	980	—	—	—	—
				75	600	3100	750	69	320,000–8	—	2.3
				150	900	3000	640	51	260,000–8	—	3.0
No. 7 *m*-fluorostyrene	75:25	—	1.75	45	700	2825	840	—	—	—	—
				75	1050	2700	700	110	2,000,000–2	—	4.2+
				150	1000	2200	550	—	—	—	—
GR-S control	—			Same as that under No. 5 *p*-chlorostyrene							
No. 8 *p*-fluorostyrene	75:25	—	2.0	45	425	2725	795	—	—	—	—
				75	700	3400	710	77	400,000–8	—	2.2
				150	825	2800	550	57	270,000–8	—	2.7
GR-S control	—			Same as that under No. 5 *p*-chlorostyrene							
No. 9 *o*-bromostyrene	75/25	—	1.75	75	1200	2850	525	60	320,000–8	—	2.9
				150	1500	2650	465	53	210,000–8	—	2.3
GR-S control	—	—	1.75	75	950	2800	575	57	410,000–8	—	4.1
				150	1300	3050	525	46	290,000–8	—	4.0
No. 10 *m*-bromostyrene	75:25	—	1.75	75	1400	2750	450	67	170,000–8	—	1.2
				150	1700	2700	410	51	170,000–8	—	2.0
GR-S control	—			Same as that under No. 1 *o*-chlorostyrene							
No. 11 *p*-bromostyrene	75:25	—	2.0	45	250	2350	980	—	—	—	—
				75	725	2700	700	98	280,000–8	—	0.8
				150	925	3000	600	66	180,000–8	—	1.3
GR-S control	—	—	Same as that under No. 6 mixed monochlorostyrenes								
No. 12 2,3-dichlorostyrene	75:25	25	1.75	75	710	3700	715	71	260,000–8	60	1.7
				150	920	3790	655	51	250,000–8	62	3.0
GR-S control	—	—		Same as that under No. 2 *o*-chlorostyrene							
No. 13 2,4-dichlorostyrene	75:25	—	2.0	45	450	2300	780	—	—	—	—
				75	750	2900	610	85	330,000–8	—	1.4
				150	1050	2850	530	58	180,000–8	—	1.7
GR-S control	—	—		Same as that under No. 5 *p*-chlorostyrene							
No. 14 2,5-dichlorosytrene	75:41.6	—	1.75	45	1200	3400	635	—	—	—	—
				75	—	2900	475	99	1,450,000–8	—	4.2
				150	2000	3100	465	—	—	—	—

TABLE V—*Continued*

Comonomer	Ratio, butadiene: comonomer	Mooney viscosity*	Sulfur (parts)	Cure (min. at 280° F)	300% modulus (lbs. per sq. in.)	Tensile (lbs. per sq. in.)	Elongation (%)	Hysteresis temp. rise (° F)	Flexing†	Durometer hardness	Quality index[15]
GR-S control	—	—		Same as that under No. 5 *p*-chlorostyrene							
No. 15 2,6-dichlorostyrene	75:25	—	1.75	.75	1200	2450	505	62	110,000–8	—	0.9
				150	1450	2050	390	56	100,000–8	—	1.0
GR-S control	—	—		Same as that under No. 9 *o*-bromostyrene							
No. 16 3,4-dichlorostyrene	75:41.6	—	—	45	850	3275	610	83	1,950,000–8	—	9.2
				60	1175	3750	610	—	—	—	—
GR-S control	—	—		Same as that under No. 5 *p*-chlorostyrene							
No. 17 3,4-dichlorostyrene	85:15	59	1.75	75	800	3540	674	86	300,000–8	63	1.3
				150	1000	3470	607	74	270,000–8	63	1.7
GR-S control	—	—		Same as that under No. 3 *o*-chlorostyrene							
No. 18 3,5-dichlorostyrene	75:25	23	2.0	75	680	3300	733	98	1,560,000–8	63	4.8
				150	940	3300	627	83	750,000–8	67	3.5
GR-S control	—	—	2.0	75	740	3250	713	97	960,000–8	53	3.0
				150	940	3740	674	66	420,000–8	57	3.2
No. 19 mixed chlorostyrenes	75:25	—	2.0	45	400	2500	880	—	—	—	—
				75	800	3400	695	89	950,000–8	—	3.7
				150	1200	2800	480	73	320,000–8	—	2.0
GR-S control	—	—		Same as that under No. 4 *m*-chlorostyrene							
No. 20 mixed trichlorostyrenes	75:25	—	1.75	75	550	2850	725	98	340,000–8	—	0.9
				150	675	3000	700	64	240,000–8	—	1.9
GR-S control	—	—		Same as that under No. 1 *o*-chlorostyrene							
No. 21 mixed tetrachlorostyrenes	75:25	48	2.0	75	1030	2900	607	65	120,000–8	57	0.92
				150	1330	3150	513	56	70,000–8	61	0.71
GR-S control	—	45	2.0	75	950	3020	648	58	640,000–8	62	6.1
				150	1100	1990	433	50	330,000–8	63	4.0
No. 22 *p*-cyanostyrene	75:25	26	1.75	75	1120	3150	580	83	2,000,000–5	67	9.2+
				150	1180	3200	540	102	1,660,000–8	76	4.4
GR-S control	—	—		Same as that under No. 2 *o*-chlorostyrene							

appear to be somewhat superior to GR-S, and those of *m*-chlorostyrene and *m*-fluorostyrene may possibly be superior.

2. Copolymers of the dichlorostyrenes, with the exception of the 2,5- and 3,4-, give quality indexes about equal to that of GR-S. These two isomers, particularly the latter, show an appreciable improvement. Since the rate of entry of these materials into the polymer during polymerization is greater than that of styrene, the combined halogenated styrene content is greater than that of the styrene in GR-S. Comparison should, therefore, be made with butadiene-styrene copolymers having an equivalent styrene content, since an increased styrene content results in an improvement in quality index[15].

3. The mixed tri- and tetrachlorostyrenes are both definitely inferior to styrene.

4. The *p*-cyanostyrene copolymer gave a high quality index and good stress-strain properties. However, from its composition it would be anticipated that its low temperature properties would be poor.

These conclusions are based on the results obtained in copolymers made in the particular recipe given and may or may not apply to copolymers made ni other polymerization systems. In several cases the Mooney viscosity of the copolymer differed wide from that of standard GR-S. Had it been possible to adjust the viscosity of the product to that of standard GR-S, the results and conclusions might have been somewhat different.

SUMMARY

Butadiene has been copolymerized in a typical emulsion polymerization recipe with each of the monochloro-, monobromo-, monofluoro-, and dichlorostyrenes, with the mixed mono-, di-, tri-, tetra-, and pentachlorostyrenes, and with *p*-cyanostyrene and several of its derivatives. While 2,5- and 3,4-dichlorostyrene copolymerized with butadiene more rapidly than does styrene itself, 2,6-dichlorostyrene and the mixed tri-, tetra-, and pentachlorostyrenes copolymerized at a slower rate than did the control. 2,5-Dichlorostyrene entered the copolymer much more rapidly, and 2,6-dichlorostyrene and pentachlorostyrene much more slowly, then does styrene itself. The mono- and dihalogenated styrenes in general gave copolymers whose quality indexes were about equal to that of GR-S; *o*-chlorostyrene, 2,5- and 3,4-dichlorostyrenes, and *p*-cyanostyrene all gave copolymers with quality indexes higher than that of GR-S. The mixed tri- and tetrachlorostyrenes gave copolymers of inferior quality.

REFERENCES

[1] Clifford, A. M., and D'Ianni, J. D., private communication, Charpmael (I. G. Farbenindustrie A.-G), British patent 387,381 (1933); Michalek and Clark, *Chem. Eng. News* **22**, 1559 (1944).
[2] Marvel, Overberger, Allen, Johnson, Saunders and Young, *J. Am. Chem. Soc.* **68**, 861 (1946).
[3] Wall, *J. Am. Chem. Soc.* **63**, 1862 (1941).
[4] Pierson, R. M., private communication.
[5] Brooks, *J. Am. Chem. Soc.* **66**, 1295 (1944).
[6] Brown and Marvel, *J. Am. Chem. Soc.* **59**, 1176 (1937); Marvel and Moon, *J. Am. Chem. Soc.* **62**, 45 (1940); Marvel and Schertz, *J. Am. Chem. Soc.* **65**, 2054 (1943).
[7] Biltz, *Ann.* **296**, 259 (1897).
[8] Emerson and Agnew, *J. Am. Chem. Soc.* **67**, 518 (1945).
[9] Levine and Cass, U. S. patents 2,290,759 (1943) and 2,193,823 (1940).
[10] Marvel and Overberger, *J. Am. Chem. Soc.* **67**, 2250 (1945).
[11] Laitinen, Miller and Parks, *J. Am. Chem. Soc.*, in press.
[12] Hulse, Hobson, Wall, Johnson, Yanko and Flory, private communication.
[13] Garvey, *Ind. Eng. Chem.* **34**, 1932 (1942).
[14] Lessig, *Ind. Eng. Chem. Anal. Ed.* **9**, 582 (1937).
[15] Juve, *Ind. Eng. Chem.* **39**, 1494 (1947).

PROPERTIES OF POLYCHLOROPRENE MOLECULES IN SOLUTION *

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Chloroprene can polymerize to polymers of five different types, α-, β-, μ-, ω- and balatalike polymers. This was pointed out by Carothers, Williams, Collins, and Kirby[1] in their very first paper on chloroprene and its polymerization products. From a technical point of view only two of these types are of interest, namely, the α- and μ-polymers. The α-polymer is formed during the first stages in the polymerization, and pure α-polymer can be obtained only if the reaction is interrupted before 20 to 30 per cent of the chloroprene has polymerized. The formation of α-polymer is assumed to be an ordinary polymerization reaction, and the macromolecules are probably chains of great length. If larger amounts than 20 to 30 per cent of the chloroprene have polymerized, the α-polymer is partly converted into μ-polymer. This seems to be a process of cross-linking, and hence the molecules formed must be quite different in shape from those of ω-polymer.

Now the polymerization process can be performed either in chloroprene-water emulsion or as bulk polymerization. In the first case the system is a very complicated one, but it is possible to convert up to 80 per cent of the chloroprene to a high polymeric product. It is, however, very difficult to say anything about the type of polymer formed. It is probably a mixture of α- and μ-polymers in different proportions. As in homogeneous polymerization, the reaction must be interrupted at an early stage, the conditions seem favorable for the formation of pure α-polymer. If a large number of polymerizations are carried out, it is obvious that one can obtain products corresponding to polymers with different molecular properties. It is the purpose of this paper to give an account of ultracentrifugal measurements on different polychloroprenes and to demonstrate a fundamental difference between molecules formed by emulsion polymerization and bulk polymerization.

MATERIALS INVESTIGATED

The polymers used were obtained from polymerization both on a laboratory scale and in a pilot plant. The polymerization was carried out from freshly distilled chloroprene, with a peroxide catalyst. In the case of emulsion polymerization, the emulsifying agent was ammonium oleate. Sulfur was often used as a modifier. After polymerization the unpolymerized chloroprene in bulk polymerization was evaporated in a special apparatus, and in emulsion polymerization the polymer was precipitated from the latex. In both cases the polymers were stabilized with a stabilizing agent. The notations A- and B-polymers have been introduced for polymers from emulsion and bulk polymerization, respectively.

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* Reprinted from the Harald Nordenson 60th Anniversary Volume, 1946, pages 321–339.

In the measurements, chloroform with a specific gravity of 1.486 was used as a solvent. Since some of the polymers, especially from emulsion polymerization, were only partially soluble, determinations of the solubility were carried out in all cases. If the solubility was less than 100 per cent, the molecular weight was determined on the soluble fraction.

The partial specific volume V necessary for molecular-weight calculations according to Equation (4) has been determined pycnometrically. For different polymers and different solvents the values obtained show no variation, and a mean value of $V = 0.795$ has been found[2].

The polymers show some alteration with time, and to eliminate this effect, all measurements—both sedimentation and diffusion—were carried out within a time interval in which the alterations are negligible.

SEDIMENTATION MEASUREMENTS

For the principles of sedimentation in the ultracentrifuge the reader is referred to the work of Svedberg and Pedersen[3]. The scale method of Lamm[4] was used, and the speed of the rotor was 40,000–55,000 r.p.m., depending on the magnitude of the sedimentation constant. This corresponds to a centrifugal force of 120,000–220,000 grams. Within the limits the speed of the rotor has no influence on the sedimentation behavior of the substances. It may be pointed out that the substances sedimentate towards the center of rotation, since the specific gravity of chloroprene is less than that of chloroform.

According to an investigation by Mosimann[5], the stabilizing agent can be removed from the polymer by precipitating the material several times; it is, therefore, not chemically bound to the polychloroprene molecule. Thus the stabilizing agent cannot have any appreciable influence on the refractive index

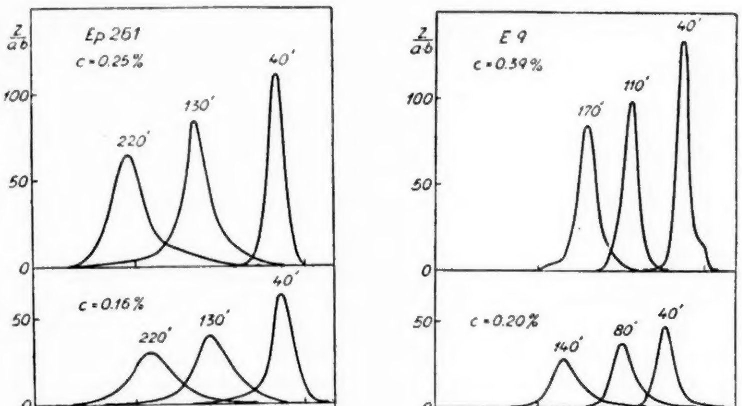

FIG. 1.—Sedimentation curves of A-polymers. Left: Ep 261 at a rotor speed of 54,000 (0.25%) 45,000 (0.16%) and 40,000 (0.10%) r.p.m. Right: E 9 at a rotor speed of 54,000 r.p.m. Abscissa: distance from center of rotation (cm.).

gradient of the polychloroprene solution. This justifies the measurements being carried out with the stabilizing agent present.

The sedimentation diagrams always show one peak, which, however, especially at small concentrations, becomes very low and wide. For this reason it is impossible to use concentrations smaller than 0.1 per cent. In Figures 1 and 2, sedimentation diagrams for A- and B-polymers at different concentrations are shown. The extrapolation of s to zero concentration has been made either in a (s, c)-diagram or a (s, s, c)-diagram. It has been found that in many cases the variation of s with c follows equation of Gralén[6]:

$$s = s_0/(1 + k\cdot c) \tag{1}$$

The measurements on polychloroprenes from emulsion polymerization are given in Table 1, and those from bulk polymerization in Table 2. The concentration

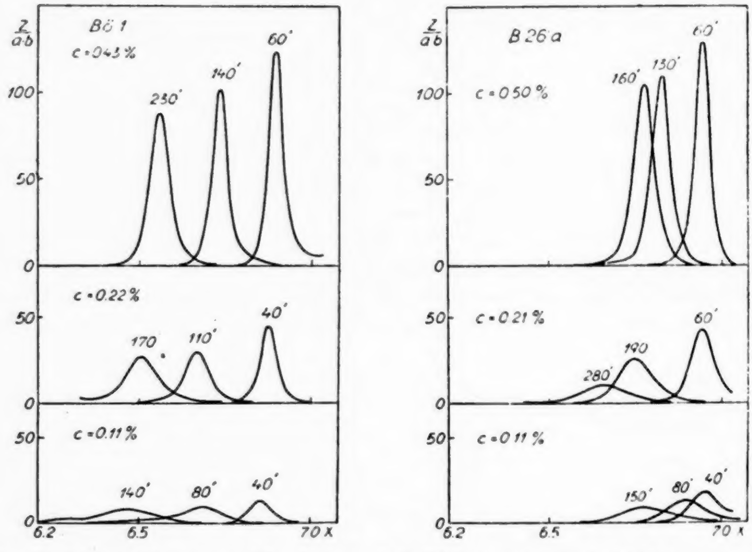

FIG. 2.—Sedimentation curves of B-polymers. Left: Bö 1 at a rotor speed of 54,000 r.p.m. Right: B 26a at a rotor speed of 54,000 (0.50%) and 40,000 (0.21%; 0.11%) r.p.m. Abscissa: distance from center of rotation (cm.).

is expressed in percentage by weight, and the sedimentation constant in S units. The s-values are referred to a temperature of 20° C. Some examples of the variation of s with c are shown in Figures 3 and 4. The curves of the A-polymers are steeper than those of the B-polymers. It also follows from the k-values in Tables 1 and 2 that the concentration dependence of the A-polymers is greater than that of the B-polymers. Thus the percentage number of k-values exceeding $k = 5$ is 30 for A-polymers and 13.5 for B-polymers.

It is a striking fact that the sedimentation constants of the B-polymers show very small variations. This is seen more clearly from Figure 5, where the number n of s-values in an interval of the magnitude 0.24 S are plotted against s. The shaded piles correspond to B-polymers and the others to A-polymers. It is evident that the distribution for B-polymers shows a maximum at about 3.5 S, whereas the s-values of A-polymers are more uniformly spread over the whole axis.

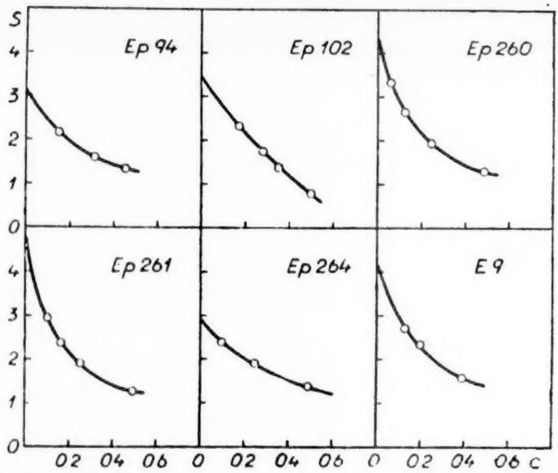

Fig. 3.—The sedimentation constant of A-polymers as a function of concentration.

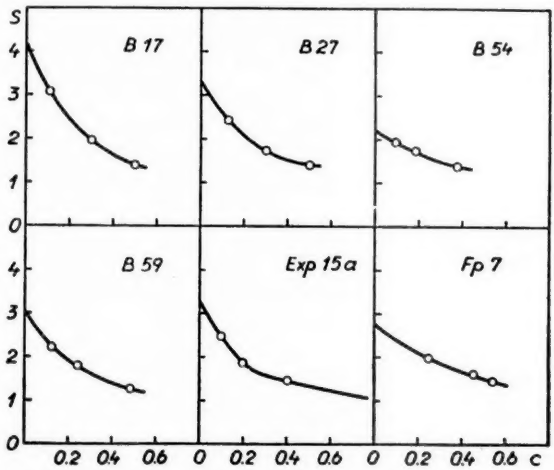

Fig. 4.—The sedimentation constant of B-polymers as a function of concentration.

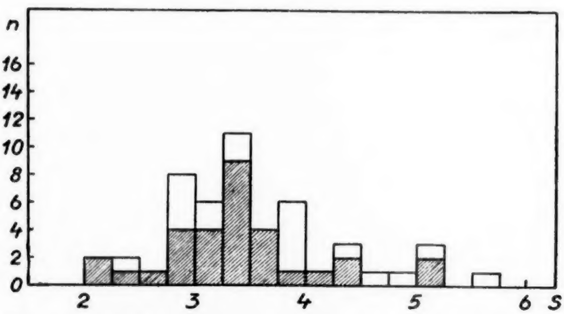

Fig. 5.—Number n of s-values in interval of 0.24 S as a function of s.

Table 1

Sedimentation Behavior of A-Polymers

Sample	Solubility %	c	c. s	s	k
Ep 11	100	2.07	—	0.60	—
		0.90	—	1.00	—
		0.35	0.59	1.68	1.00
		0.17	0.32	1.97	0.90
		0.08	0.17	2.11	0.97
		0		2.3	1.0
Ep 79:1	100	0.79	0.82	1.04	2.08
		0.35	0.57	1.64	1.94
		0.23	0.43	1.86	2.08
		0		2.8	2.0
Ep 79:2	100	0.66	0.81	1.23	4.33
		0.35	0.66	1.88	4.37
		0.23	0.55	2.38	4.33
		0		4.8	4.3
EP 94	100	0.45	0.60	1.34	2.83
		0.31	0.49	1.58	3.00
		0.15	0.32	2.14	2.83
		0		3.1	2.9
Ep 97	46	0.46	0.64	1.38	2.55
		0.30	0.54	1.79	2.26
		0.10	0.24	2.41	2.47
		0		3.0	2.4
Ep 102	15	0.50		0.79	
		0.35		1.39	
		0.28		1.73	
		0.17		2.30	
		0		3.5	
Ep 120	100	0.33		2.15	
		0.20		2.65	
		0.10		2.83	
		0		3.3	
Ep 253	100	0.49		1.48	
		0.25		2.00	
		0.11		2.98	
		0		4.1	
Ep 254	100	0.48		1.28	
		0.24		1.94	
		0.12		2.85	
		0		4.0	
Ep 258	100	0.51		1.34	
		0.25		1.66	
		0.13		2.52	
		0		3.1	
Ep 260	100	0.49	—	1.30	—
		0.24	0.47	1.93	5.27
		0.12	0.32	2.63	5.56
		0.06	0.20	3.32	5.50
		0		4.4	5.4
Ep 261	100	0.49	—	1.27	—
		0.25	0.47	1.88	6.04
		0.16	0.38	2.36	6.24
		0.10	0.30	2.92	6.31
		0		4.7	6.1
Ep 262	100	0.50		1.13	
		0.25		1.81	
		0.10		2.29	
		0		2.8	
Ep 263	100	0.47	0.60	1.28	6.28
		0.23	0.46	2.00	6.56
		0.09	0.30	3.18	6.23
		0		5.0	6.4
Ep 264	100	0.49	0.68	1.38	2.32
		0.25	0.46	1.87	2.34
		0.10	0.24	2.40	2.32
		0		3.0	2.3
Ep 266	100	0.52		1.07	
		0.34		1.52	
		0.17		1.92	
		0		2.8	
E 8	10	0.20		2.63	
		0.10		2.95	
		0.07		3.30	
				4.0	
E 9	39	0.39	0.62	1.58	4.26
		0.20	0.44	2.23	4.43
		0.13	0.35	2.70	4.28
		0		4.2	4.3
E 15	100	0.28		2.17	
		0.18		2.79	
		0.11		3.75	
		0		5.5	

TABLE 2

SEDIMENTATION BEHAVIOR OF B-POLYMERS

Sample	Solubility %	c	c. s	s	k
B 17	100	1.00	0.86	0.86	4.12
		0.50	0.70	1.40	4.28
		0.30	0.59	1.97	4.10
		0.10	0.33	3.07	4.13
		0	—	4.4	4.1
B 18a	100	2.05		0.50	
		1.05		0.83	
		0.21		2.01	
		0.11		2.69	
		0		3.5	
B 26a	100	0.50	0.64	1.28	3.53
		0.21	0.43	2.05	3.48
		0.11	0.28	2.55	3.56
		0		3.6	3.5
B 27	100	0.50		1.41	
		0.25		1.72	
		0.13		2.45	
		0		3.3	
B 48a	100	0.56		1.13	
		0.28		1.91	
		0.14		2.35	
		0		3.1	
B 48b	100	0.61		1.11	
		0.31		1.60	
		0.15		2.36	
		0		3.4	
B 54	76	0.37	0.52	1.39	1.56
		0.19	0.32	1.72	1.50
		0.09	0.18	1.93	1.50
		0		2.2	1.5
B 57	55	0.57		0.47	
		0.28		1.02	
		0.14		1.38	
		0		2.0	
B 58	94	0.47	0.57	1.21	2.45
		0.24	0.37	1.58	2.75
		0.22	0.24	2.05	2.28
		0		2.6	2.5
B 59	92	0.48	0.60	1.25	2.91
		0.24	0.43	1.79	2.82
		0.12	0.27	2.21	2.99
		0		3.0	2.9
Exp 15a	100	0.80		1.05	
		0.40		1.46	
		0.20		1.86	
		0.10		2.47	
		0		3.3	
Exp 15b	100	0.48		0.85	
		0.24		1.17	
		0.10		1.64	
		0		2.3	
Fp 1	100	1.00		0.97	
		0.50		1.53	
		0.20		2.09	
		0		2.8	
Fp 4	100	1.63	1.04	0.64	2.70
		1.17	0.91	0.78	2.92
		0.30	0.56	1.88	2.80
		0.15	0.36	2.45	2.82
		0		3.5	2.8
Fp 7	91	0.55	0.79	1.45	1.64
		0.45	0.73	1.62	1.55
		0.25	0.50	1.97	1.57
		0		2.6	1.6
TPO 3	100	2.40	1.18	0.49	2.31
		1.55	1.09	0.70	2.31
		1.04	0.95	0.91	2.38
		0.53	0.75	1.44	2.33
		0.39	0.63	1.63	2.49
		0.25	—	2.28	—
		0		3.2	2.4
TPO 4	100	2.12		0.55	
		1.45		0.68	
		1.12		0.86	
		0.45		1.38	
		0.25		2.56	
		0.14		2.93	
		0		3.4	
Bö 1	100	0.87	0.80	0.92	3.86
		0.43	0.62	1.45	4.11
		0.22	0.50	2.25	3.58
		0.11	0.31	2.78	4.06
				4.0	3.9

TABLE 2—*Continued*

Sample	Solubility %	c	$c.s$	s	k
Bö 3	100	0.48		1.40	
		0.32		1.73	
		0.31		1.69	
		0.16		2.12	
		0.10		2.71	
		0		3.3	
Bö 6	100	0.35		1.80	
		0.25		2.16	
		0.17		2.26	
		0		3.3	
Bö 7	100	0.96	0.82	0.85	2.81
		0.48	0.64	1.32	2.88
		0.12	0.28	2.35	2.82
		0.06	0.16	2.69	2.80
		0		3.1	2.8
Bö 9	100	0.55		1.16	
		0.27		1.90	
		0.10		2.52	
		0		3.3	
Bö 10	100	0.41	0.60	1.47	5.91
		0.21	0.46	2.24	6.10
		0.10	0.32	3.19	5.69
		0.10	0.31	3.16	5.85
		0		5.0	6.0
Bö 20	86	0.42		1.29	
		0.21		1.87	
		0.10		1.95	
		0		2.8	
Bö 21	100	0.40	0.66	1.62	1.76
		0.20	0.40	1.99	1.94
		0.10	0.24	2.38	1.61
		0		2.8	1.8
Bö 22	91	0.45		1.52	
		0.22		1.97	
		0.11		2.72	
		0		3.7	
Bö 23	97	0.49		1.23	
		0.24		1.52	
		0.12		2.19	
		0		3.3	
Bö 24	95	0.40		1.74	
		0.20		2.31	
		0.10		2.53	
		0		3.5	
Bö 26	100	0.50	0.72	1.43	3.99
		0.25	0.52	2.06	4.36
		0.13	0.37	2.90	3.89
		0		4.3	4.1
BLjv:h	100	1.12	0.85	0.76	3.75
		0.28	0.54	1.93	3.75
		0.10	0.29	2.86	3.78
		0		4.0	3.8
BLjv:n	100	0.88	0.82	0.93	5.29
		0.44	0.69	1.56	5.38
		0.11	0.37	3.31	5.30
		0		5.2	5.3
ANE	100	0.50		1.38	
		0.30		1.95	
		0.10		2.69	
		0		3.3	

DIFFUSION MEASUREMENTS

The diffusion measurements in chloroform solution were very difficult to perform. The levelling of the pure chloroform under the polychloroprene solution and the packing of the cocks in the diffusion cell with a suitable lubricant were the main problems. As lubricant a paste made up of glycerol and dextrin recommended by Kaspenberg[7] was used. Another problem was the influence of low-molecular compounds, such as the stabilizing agent. Since according to Mosimann's investigation this substance is not chemically bound to the macromolecules, its influence on the diffusion process must be most pronounced during the first few hours after the levelling. Thus all calculations of the diffusion coefficients were made such a long time after the beginning of the diffusion process (about five hours), that the concentration of the stabilizing agent could be assumed to be constant throughout the whole cell.

The diffusion measurements were carried out in a glass cell, and Lamm's scale method[4] was used. The diffusion curves show in some cases a more or less pronounced skewness, but the displacement of the maximum point is not regular, and any calculation of D_0-values by Gralén's method[6] cannot be made. The calculations have been made according to the area method:

$$D_A = A^2/4\pi t H^2 \tag{2}$$

and the moment method:

$$D_m = \sigma^2/2t \tag{3}$$

where A is the area and H the height of the curve, and $\sigma^2 = m_2/A$, where m_2 is the second moment of the curve. The quantities $(A/H)^2/t$ and σ^2/t were determined from diagrams where $(A/H)^2$ and σ^2 are plotted against the time t. Corresponding points should theoretically lie on straight lines through the origin. The linear relationship is evident. The lines, however, do not in all cases pass through the origin, but cross the t-axis at a certain negative or positive time. This is exemplified in Figure 6, where Exp 15a and Ep 261 cross

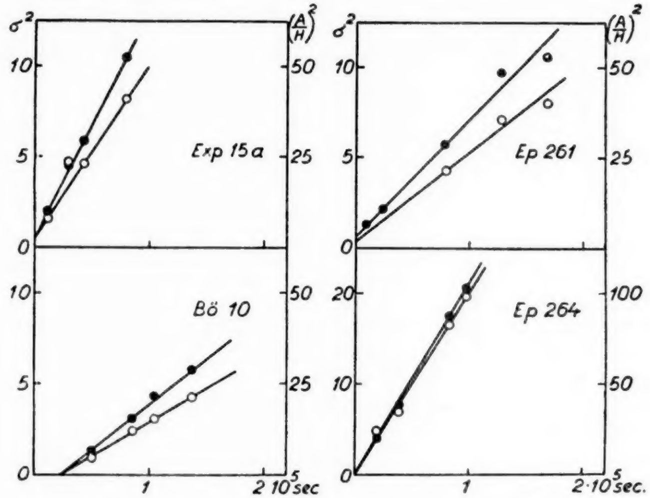

FIG. 6.—The standard deviation σ^2 (in mm.^{2}) and the quotient $(A/H)^2$ (in mm.^{2}) as functions of time.

the t-axis at a negative time, Ep 264 passes through the origin and Bö 10 crosses the t-axis at a positive time. A negative intercept on the t-axis is most likely due to some disturbance in connection with the levelling procedure. A positive intercept is in this case more difficult to understand, and any true explanation has not been found. Gralén found the same phenomenon for different celluloses in cuprammonium, and his opinion is that part of the effect may be attributed to some depolymerization, or that the complexity of the solution may cause an increase of the diffusion coefficient during the beginning of the experiments. In our case it is very unlikely that such phenomena should occur.

It is very difficult to perform a diffusion experiment at small concentrations, and hence no accurate extrapolation to zero concentration can be made. The determinations have been carried out at one or two concentrations. The values

TABLE 3

DIFFUSION COEFFICIENTS OF POLYCHLOROPRENES

A-Polymers

Sample	c	D_m	D_A
Bö 26	0.11	—	0.5
BLjv:n	0.50	4.7	4.2
BLjv:h	0.25	1.8	1.6
Ep 11	0.59	4.2	3.8
Ep 79:1	0.30	2.7	(4.4)
Ep 79:2	0.25	—	2.7
Ep 94	0.50	3.5	3.4
Ep 97	0.30	—	3.8
Ep 102	0.14	—	(4.8)
Ep 120	0.50	1.4	1.7
Ep 253	0.11	3.0	3.4
Ep 254	0.11	2.7	2.6
Ep 258	0.12	2.0	2.0
Ep 260	0.11	4.9	4.6
Ep 261	0.11	2.4	2.5
Ep 262	0.12	0.6	0.5
Ep 263	0.16	4.1	3.4
Ep 264	0.12	9.8	8.3
Ep 266	0.25	3.2	3.5
	0.15	3.7	3.9
E 8	0.39	3.4	3.3
E 9	0.30	2.3	3.6
E 15	0.55	3.3	3.6

B-Polymers

Sample	c	D_m	D_A
B 17	0.30	1.2	1.2
B 18a	0.50	2.3	—
	0.30	(3.1)	2.9
B 26a	0.50	2.6	2.8
B 27	0.50	2.3	2.8
B 48a	0.56	—	2.0
B 48b	0.31	1.1	1.1
	0.61	—	2.8
Exp 15a	0.32	4.6	4.9
Exp 15b	0.32	4.8	4.6
	0.10	—	5.6
Fp 4	0.29	3.8	3.4
Fp 7	0.45	2.7	2.7
TPO 3	0.53	(4.6)	3.4
TPO 4	0.45	2.7	2.8
Bö 1	0.50	—	(4.7)
Bö 3	0.50	2.1	2.1
	0.30	1.7	1.9
Bö 6	0.50	—	2.4
	0.30	—	3.0
Bö 7	0.50	3.1	3.0
	0.25	1.9	2.5
Bö 9	0.55	—	3.6
	0.27	2.7	3.8
Bö 10	0.41	—	1.6
	0.21	1.9	2.1
Bö 20	0.30	5.4	6.0
	0.15	2.7	3.2
ANE	0.50	2.24	2.25
	0.30	2.11	2.50

found are recorded in Table 3, where the concentration is expressed in percentage by weight and the diffusion coefficients in units of 10^{-7} sq. cm. per sec. at a temperature of 20° C.

Compared with the sedimentation constants, the diffusion coefficients show no similar distribution either for A- or B-polymers. For the B-polymers the sedimentation constant seems to be rather independent of the diffusion coefficients. This is seen in Figure 7, where s has been plotted against D.

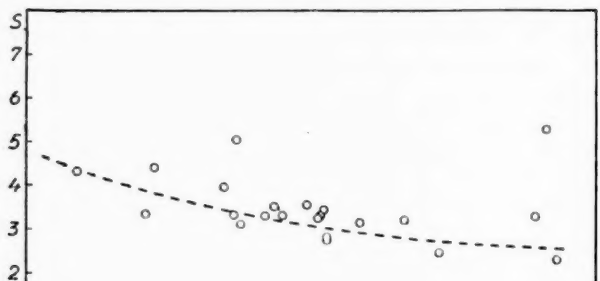

FIG. 7.—The sedimentation constant as a function of the diffusion coefficient for B-polymers.

MOLECULAR WEIGHT AND SHAPE OF THE MOLECULES

For a monodisperse substance the molecular weight M can be calculated from the formula of Svedberg[8]:

$$M = \frac{RTs}{(1 - V\rho)D} \tag{4}$$

In the case of polydispersity (polymolecularity), one can characterize the substance by means of different average molecular weights. Integrating Equation (4) over the whole range of molecular species, one gets for the weight average molecular weight:

$$M_w = \frac{RT}{(1 - V\rho)c_0} \int_o^{c_0} \frac{sdc}{D} \tag{5}$$

in the partial specific volume is independent of the particle size. It is impossible to determine the integral in (5) from separate diffusion and sedimentation experiments. Jullander[9] has shown that a molecular weight calculated from (4) with a weight average value s_w and a D_m-value, *i.e.*:

$$M_{w,w} = \frac{RTs_w}{(1 - V\rho)D_m} \tag{6}$$

does not coincide with the value M_w from Equation (5). Furthermore, the value s_0 obtained from a sedimentation experiment is not a well defined average value of s. Within the limits of experimental error one can, however, estimate that s_0 characterizes the main part of the sedimentating substance. If the sedimentation curves are not too skew, the molecular weight calculated from s_0 and D_m is close to $M_{w,w}$[10].

TABLE 4

MOLECULAR WEIGHTS OF POLYCHLOROPRENES

A-Polymers				B-Polymers			
Sample	s_0	D_m	M	Sample	s_0	D_m	M
Ep 264	3.0	9.8	40,500	Exp 15b	2.3	4.8	62,000
Ep 11	2.3	4.2	72,500	Fp 4	2.5	3.8	87,000
Ep 102	3.5	*4.8	96,000	Exp 15a	3.3	4.6	94,000
Ep 97	3.0	*3.8	106,000	Bö 1	4.0	*4.7	115,000
Ep 266	2.8	3.4	108,000	TPO 3	3.2	*3.4	125,000
Ep 94	3.1	3.5	117,000	Fp 7	2.8	2.7	135,000
Ep 260	4.4	4.9	120,000	Bö 20	2.8	2.7	137,000
Ep 79:1	2.8	2.7	136,000	Bö 7	3.1	3.0	139,000
E 8	4.0	3.4	157,000	BLjv:n	5.2	4.7	148,000
Ep 263	5.0	4.1	164,000	Bö 9	3.3	2.7	164,000
Ep 253	4.1	3.0	185,000	Bö 6	3.3	*2.7	166,000
Ep 254	4.0	2.7	198,000	TPO 4	3.4	2.7	170,000
E 15	5.5	3.3	223,000	B 26a	3.6	2.6	186,000
Ep 79:2	4.8	*2.7	235,000	B 27	3.3	2.3	190,000
E 9	4.2	2.3	242,000	ANE	3.3	2.2	204,000
Ep 261	4.7	2.4	261,000	B 18a	3.5	2.3	208,000
Ep 258	4.1	2.0	274,000	B 48a	3.1	2.0	213,000
Ep 120	3.3	1.4	313,000	Bö 3	3.3	1.9	234,000
Ep 262	2.8	0.6	657,000	BLjv:h	4.0	1.8	294,000
				Bö 10	5.0	1.9	353,000
				B 48b	3.4	1.1	415,000
				B 17	4.4	1.2	508,000
				Bö 26	4.3	*0.5	1,260,000

* D_A-value.

The molecular weights of the polymers (Table 4) have been calculated in this manner from the values of s and D in Tables 1–3. If D_m is not determined, the D_A-value is used. This can be justified by the fact that the ratio D_m/D_A is in general almost equal to 1.

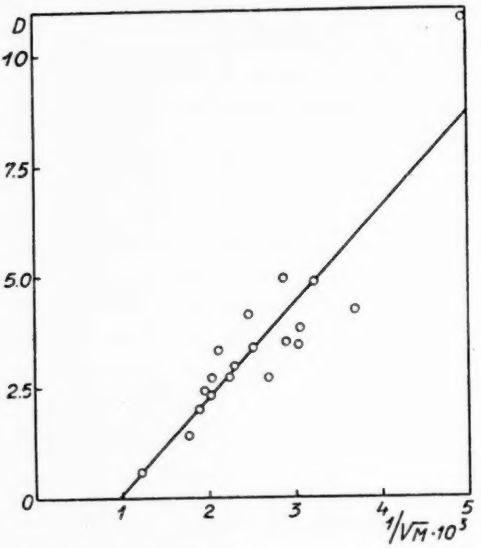

FIG. 8.—The diffusion coefficient D as a function of $1/\sqrt{M}$ for A-polymers.

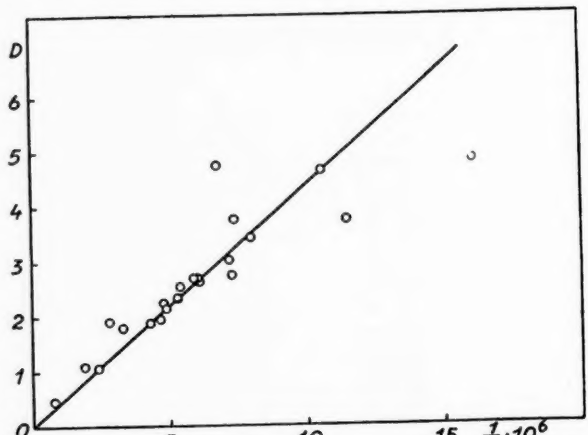

FIG. 9.—The diffusion coefficient D as function of $1/M$ for B-polymers.

A comparison of the molecular weights with the diffusion coefficients shows that a linear relationship between D and $1/\sqrt{M}$ for the A-polymers and between D and $1/M$ for the B-polymers seems to exist. This is seen from Figures 8 and 9. From the lines in the figures the following relations are obtained, for

A-polymers:

$$D = -2.0\cdot 10^{-7} + 2.1\cdot 10^{-4}(1/\sqrt{M}) \tag{7}$$

and for B-polymers:

$$D = 4.4\cdot 10^{-2}(1/M) \tag{8}$$

The shape of the molecules is characterized by means of the frictional ratio f/f_0, the length l, and the diameter d of the molecules. The frictional ratio has been calculated from the equation:

$$f/f_0 = \frac{1}{\eta}\left(\frac{R^2T^2(1 - V\rho)}{162\pi^2N^2D^2Vs}\right)^{\frac{1}{3}} \tag{9}$$

where η is the viscosity of the solvent and N the Avogadro number. If the molecules are assumed to be unhydrated and have the shape of oblong ellipsoids of rotation with the axial ratio $l/d = 1/p$, the following equation[11] is valid:

$$f/f_0 = \frac{\sqrt{1 - p^2}}{p^{\frac{2}{3}}\log\dfrac{1 + \sqrt{1 - p^2}}{p}} \tag{10}$$

The values of l and d are related to the molecular weight and the partial specific volume by the equation:

$$\frac{\pi l d^2}{6} = \frac{M\cdot V}{N} \tag{11}$$

From Equations (10) and (11), l and d have been calculated. The values obtained are given in Table 5, where l and d are expressed in Å units. In Figure 10 the f/f_0-values are plotted against the molecular weight. In the interval

TABLE 5

MOLECULAR SHAPE OF POLYCHLOROPRENES

A-Polymers					B-Polymers				
M	f/f_0	l/d	l	d	M	f/f_0	l/d	l	d
40,500	1.7	12	250	20	62,000	2.9	48	720	15
72,500	3.2	59	860	15	87,000	3.3	65	980	15
96,000	2.5	35	660	19	94,000	2.6	39	710	18
106,000	3.1	56	940	17	115,000	2.4	33	680	21
108,000	3.4	69	1,090	16	125,000	3.2	62	1,060	17
117,000	3.3	63	1,050	17	135,000	4.0	95	1,460	15
120,000	2.3	28	620	22	137,000	4.0	94	1,450	15
136,000	4.0	96	1,470	15	139,000	3.5	75	1,250	17
157,000	3.0	53	1,040	20	148,000	2.2	26	630	24
164,000	2.5	34	770	23	164,000	3.8	88	1,480	17
185,000	3.3	64	1,240	19	166,000	3.8	86	1,460	17
198,000	3.5	74	1,400	19	170,000	3.7	83	1,440	17
223,000	2.8	44	1,020	23	186,000	3.8	88	1,530	16
235,000	3.3	65	1,360	21	190,000	4.2	105	1,740	17
242,000	3.9	90	1,700	19	204,000	4.4	116	1,900	16
261,000	3.6	77	1,570	21	208,000	4.2	106	1,810	17
274,000	4.3	114	2,080	18	213,000	4.8	140	2,190	16
313,000	5.8	205	3,210	16	234,000	4.8	140	2,260	16
657,000	11.4	765	9,900	13	294,000	4.6	130	2,320	18
					353,000	4.1	103	2,110	21
					415,000	6.9	292	4,460	15
					508,000	6.0	223	3,990	18
					1,260,000	11.2	740	12,030	16

M = 150,000–300,000 especially, it is evident that the molecules of B-polymers are more lengthened than those of A-polymers. Below 150,000 there seems to be no difference, and above 300,000 the measurements are too few to permit any reliable comparison. From the d-values it follows that the thickness of the B-molecules is rather constant (only three values exceed 20 Å). The length of the molecules increases almost proportionally to the molecular weight. For the quotient l/M one obtains the value $(8.83 \pm 0.37) \cdot 10^{-3}$ Å. The thickness of the A-molecules varies over a wider range, and the length does not increase in the same regular manner.

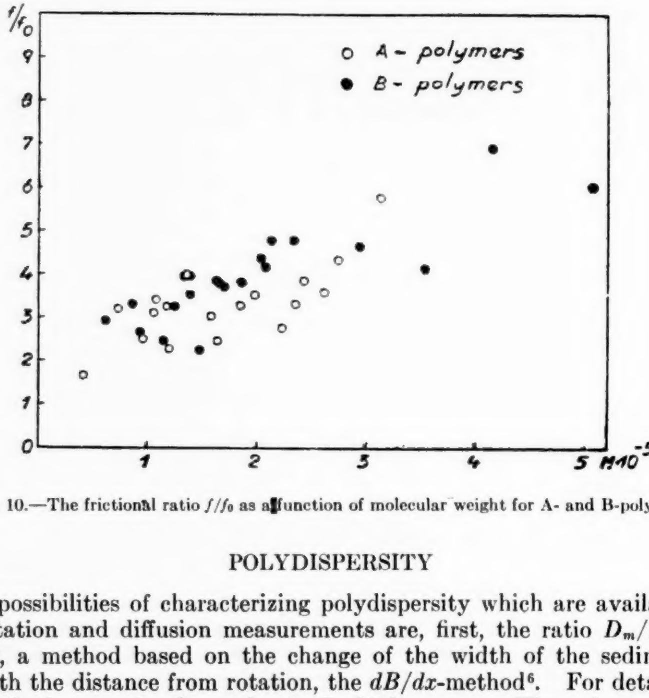

FIG. 10.—The frictional ratio f/f_0 as a function of molecular weight for A- and B-polymers.

POLYDISPERSITY

The possibilities of characterizing polydispersity which are available from sedimentation and diffusion measurements are, first, the ratio D_m/D_A[12] and, secondly, a method based on the change of the width of the sedimentation curve with the distance from rotation, the dB/dx-method[6]. For details about these methods we refer the reader to Gralén's papers. The values calculated are given in Table 6. It is immediately evident that the results from the two methods are not comparable. It must, however, be emphasized that the dB/dx-method gives the most reliable values, as the diffusion curves are both skew and in many cases anomalous. From Figure 11, where the $(dB/dx)_0$-values are plotted against the molecular weight, it is seen that the polydispersity does not show any regular variation with the average molecular weight, and hence it is not possible to say anything about the change in the frequency curve of the sedimentation constants, when the average molecular weight increases. It is, however, obvious that the A-polymers are more polydisperse than the B-polymers: 78 and 41 per cent, respectively, of the $(dB/dx)_0$-values exceed 0.5.

DISCUSSION

From the results described in the previous sections it is evident that a certain difference in properties exists between molecules of A-polymers and

TABLE 6

POLYDISPERSITY OF POLYCHLOROPRENES

A-Polymers			B-Polymers		
M	$(dB/dx)_0$	D_m/D_A	M	$(dB/dx)_0$	D_m/D_A
40,500	0.73	1.1	62,000	0.56	1.1
96,000	0.54	—	87,000	0.54	1.1
106,000	0.24	—	94,000	0.38	1.0
117,000	0.92	1.0	115,000	0.33	—
120,000	0.69	1.1	125,000	0.85	—
136,000	0.68	—	135,000	0.99	1.0
185,000	0.97	0.9	164,000	0.31	—
198,000	0.78	1.0	170,000	0.26	1.0
223,000	0.70	0.9	186,000	0.41	0.9
235,000	0.46	—	190,000	0.44	0.9
242,000	0.28	—	208,000	0.48	1.1
261,000	0.66	1.0	213,000	0.35	—
274,000	0.81	1.0	234,000	0.40	1.0
657,000	0.60	1.2	353,000	0.52	0.9
			415,000	0.24	1.0
			508,000	0.63	1.0
			1,260,000	0.70	—

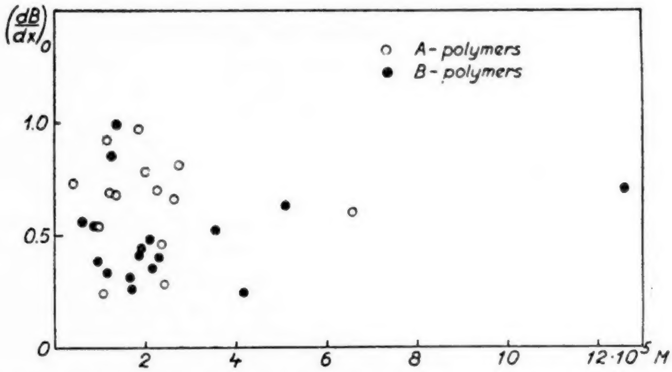

FIG. 11.—The polydispersity $(dB/dx)_0$ as a function of molecular weight for A- and B-polymers.

B-polymers. The properties of the B-molecules are well characterized by the sedimentation and diffusion data, those of the A-molecules are more difficult to interpret. Kuhn and Kuhn[13] have presumed two extreme cases for molecules moving in a solvent. Either the molecules are completely drained (*gleichmässig bespülter Faden*) or incompletely drained (*undurchspültes Knäuel*). The sedimentation and diffusion behavior of these two types of molecules are characterized by the following expressions:

Completely drained molecules:

$$s \text{ independent of } M \tag{12}$$

$$D = \text{const.}\ (l/M) \tag{13}$$

incompletely drained molecules:

$$s = \text{const.}\ \sqrt{M} \tag{14}$$

$$D = \text{const.}\ (l/\sqrt{M}) \tag{15}$$

The conditions (12) and (13) are evidently fulfilled for the B-polymers, and these molecules should, therefore, be folded, thread-shaped macromolecules. According to x-ray investigations[14] the fiber period of stretched polychloroprene is 4.79 Å. Taking this figure as the length of the monomeric molecule, one can calculate the length l_1 of a stretched macromolecule. As l/M is practically constant, the ratio l_1/l becomes independent of M, and the value is 6.1. Thus the B-molecules are folded to such an extent that in solution they are six times shorter than in the stretched state.

For the A-molecules only condition (15) seems to be fulfilled. According to (7) a correction of the diffusion coefficient must, however, be made. It is possible that the failure to fulfil condition (14) may have some connection with the different behavior of the molecules in sedimentation and diffusion experiments, and this phenomenon may depend on the branching of the chains. As a measure of the degree of branching, one can use the ratio between osmotic and viscosimetric molecular weight[15]. This ratio increases with increasing degree of branching. Probably the behavior of the molecules in sedimentation and diffusion also differs to a higher degree if the chains are highly branched.

From a technical point of view, it is of interest to mention that the B-polymers have for many purposes more favorable properties than A-polymers. This certainly depends on the differences in molecular structure. Some investigations have been made to correlate the mechanical properties of rubber with the size and shape of the macromolecules. Thus Flory[16] has observed that the tensile strength of Butyl-rubber vulcanizates is inversely proportional to the molecular weight when the concentration of cross-linkages is held constant. Any similar relationship has not been found for vulcanizates of the polychloroprenes investigated, but the failure is certainly due to the nonconstancy of the number of cross-linkages.

Lastly it must be emphasized that the material investigated is rather inhomogeneous, and this has certainly some influence on the accuracy of measurements of this kind. The difference in properties between molecules of A- and B-polymers thus may be still more pronounced, if the polymerization reactions could be held under effective control as to formation of different types of polymers. Under such circumstances it should also be possible to obtain more accurate information about the mechanical properties of the bulk material.

SUMMARY

Polychloroprenes from emulsion and bulk polymerization were investigated in the ultracentrifuge and by means of diffusion experiments. It was found that the sedimentation constants for B-polymers are independent of the polymerization conditions. This is not to the same degree the case for A-polymers. The diffusion coefficients of both types of polymers are more sensitive to differences in size of the molecules formed. A linear relationship between diffusion coefficient and the inverse value of the molecular weight has been established for B-polymers, and an inverse square root dependence for A-polymers. In the terminology of Kuhn and Kuhn, the molecules of the B-polymers should be completely drained and the molecules of the A-polymers incompletely drained. The shape of the molecules and the polydispersity of the substances are discussed. The difficulties of obtaining true and accurate values of molecular constants for such an inhomogeneous material are pointed out.

This investigation is a part of fundamental research work on synthetic

rubber carried out at the request of the Government Commission on Industry in Sweden and under the direction of Professor The Svedberg.

The authors wish to express their sincere thanks to Professor The Svedberg for his very kind interest and for the main facilities put at their disposal.

REFERENCES

[1] Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.* **53**, 4203 (1931).
[2] The authors are indebted to Professor Carl Drucker for carrying out these measurements.
[3] Svedberg and Pedersen, "The Ultracentrifuge", Oxford, **1940**.
[4] Lamm, *Nova Acta Reg. Soc. Scient. Upsaliensis* IV, **10**, No. 6 (1937).
[5] Mosimann, unpublished work.
[6] Gralén, "Sedimentation and Diffusion Measurements on Cellulose and Cellulose Derivatives", Uppsala, **1944**.
[7] Kaspenberg, *Kolloid-Z.* **86**, 18 (1939).
[8] Svedberg, *Kolloid-Z. Erg. Bd.* **36**, 53 (1925).
[9] Jullander, *Ark. Kem. Min. Geol.* **21A**, No. 8 (1945).
[10] Jullander, in "The Svedberg 1884, 30/8", **1944**.
[11] Herzog, Illig, and Kudar, *Z. physik. Chem.* **A167**, 329 (1933).
[12] Gralén, *Kolloid-Z.* **95**, 188 (1941).
[13] Kuhn and Kuhn, *Helv. Chim. Acta* **26**, 1394 (1943).
[14] Mark, in Burk and Grummit, "The Chemistry of Large Molecules", New York, **1943**, p. 64.
[15] Weidlein, *Chem. Eng. News* **24**, 771 (1946).
[16] Flory, *J. Am. Chem. Soc.* **67**, 2048 (1945).

EVALUATION OF SODIUM-CATALYZED COPOLYMERS OF 1,3-BUTADIENE AND STYRENE *

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Sodium-catalyzed butadiene-styrene copolymers of monomer ratio 75 butadiene:25 styrene by weight were prepared at the University of Illinois[1]. Evaluations were carried out simultaneously at The B. F. Goodrich Company and the United States Rubber Company. Preliminary studies indicated that the properties of the sodium copolymers were different in several respects from those of emulsion-polymerized copolymers of identical butadiene-styrene composition.

Evidences of differences in molecular structure have been reported[1] and undoubtedly result from different mechanisms of polymerization. The work reported here was carried out to determine the suitability of sodium-catalyzed butadiene-styrene copolymers as general-purpose synthetic rubbers, and to provide a background for studies relating structure of elastomeric materials to their physical behavior.

DESCRIPTION OF COPOLYMERS

The sodium-catalyzed copolymers evaluated in the two laboratories were all of 75 butadiene:25 styrene composition. The abbreviation S-BS, coined by the University of Illinois workers, is used hereafter to denote these copolymers.

The method of preparation of the samples which were evaluated followed either the "standard" method, the "interrupted" method, or the "increment addition of monomers" method as described by Marvel, Bailey and Inskeep[1].

The precise method of preparation of a particular sample is not given in the present report, since preliminary tests showed that, for equal intrinsic viscosity and benzene solubility, approximately equal results were obtained by the three methods of preparation.

Table I gives control data on the polymers tested. Each test sample is a blend of a number of experimental runs. Intrinsic viscosity and Mooney viscosity were determined on mill-massed blends. Gel determinations were made at the University of Illinois, and the range of solubilities for the different batches included in each test sample is reported.

The butadiene-styrene emulsion copolymers used as controls were from standard plant GR-S production. The emulsion system is persulfate-catalyzed, and the polymerization proceeds by means of a free radical mechanism. The

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TABLE I

CONTROL DATA

Code	Intrinsic viscosity	Percentage soluble in benzene	Mooney viscosity‡ at 212° F
S-BS I	4.9	90–100	79
S-BS II*	2.0	100	50
S-BS III	5.0	89–99	84
S-BS IV	3.7	89–100	98
30° C—S-BS	4.6–5.9†	86–97	—
50° C—S-BS	2.27–3.25†	89–100	62

* Polymer S-BS I refined by 15 passes on a cold tight mill.
† Represents range of intrinsic viscosities on polymers blended.
‡ Mooney viscosity at end of a 4-minute run using the large rotor.

ratio of the comonomers was 72 weight-per cent butadiene:28 weight-per cent styrene in the feed and approximately 75 butadiene:25 styrene by weight in the product. Intrinsic viscosities of the samples used varied, but in all cases approximated 2.0; all samples had essentially complete solubility. Mooney viscosities varied in the range 45–55.

A high-styrene emulsion copolymer, coded J-99, was prepared in the United States Rubber laboratory at 50° C, using the same type of polymerization GR-S recipe just described with the exception that the initial feed contained butadiene and styrene, respectively, in the weight ratio 40:60. Conversion was carried to 72 per cent of monomer charge. Accurate Mooney viscosity could not be determined because of slipping. However, it was estimated to be in the range 50–60.

Another high-styrene emulsion copolymer was prepared in the B. F. Goodrich laboratory at 50° C, in which the charging ratio of the monomers was 1 part butadiene to 1 part of styrene. The combined styrene in the finished copolymer was 47.90 per cent. In addition, the modifier was adjusted to give a Mooney viscosity of 50 ± 5 at 77 per cent conversion.

EXPERIMENTAL METHODS

The physical tests used in the evaluation work fall into four main types of classification: (1) processability, (2) stress-strain, (3) flex crack growth-hysteresis balance, and (4) low temperature flexibility. The following tread-type recipes, in parts by weight, were used in the two laboratories:

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Copolymer	100.0
EPC carbon black	50.0
Zinc oxide	5.0
Paraflux	5.0
Stearic acid	1.5
Santocure	1.2
Sulfur varied, when sample size permitted, to give optimum properties	

UNITED STATES RUBBER COMPANY

Copolymer	100.0
EPC carbon black	50.0
Zinc oxide	5.0
Bardol	5.0
Captax	1.5
Sulfur	2.0
BLE antioxidant	1.5

Evaluation tests were usually run on the crude copolymer. However, in some special cases (noted elsewhere in this paper), heat-treated and chemically softened copolymers were also evaluated.

Processability: mill compounding and fabrication.—Plasticity was measured by the method of Schultz and Bryant[2] and by the Mooney rotary disk plastometer[3]. All Mooney viscosity measurements were made at 212° F, using the large rotor. Objective laboratory processing measurements were made to evaluate mill compounding and fabrication qualities by the methods of White, Ebers, and Shriver[4]. The behavior of the rubber on cold milling was also noted. One large sample was mixed in an internal mixer maintained at 320° F.

Stress-strain.—Room temperature stress-strain properties were determined at the B. F. Goodrich laboratories, using small dumbbell specimens[5]. All other stress-strain measurements at both laboratories were made on standard dumbbell specimens. The instruments were not cross-calibrated, so determinations at the two laboratories are not necessarily comparable.

Flex crack growth–hysteresis balance.—Hysteresis temperature rise was measured at the B. F. Goodrich laboratory as the temperature rise in ° F above 212° F, using the Goodrich flexometer[6] with a 55-pound load and a $17\frac{1}{2}$ per cent stroke. Flexing results are reported by that laboratory in terms of the number of flexures required for an initial crack to go to an arbitrary rating of eight (about 75 per cent of a 1-inch width). A De Mattia machine was used, operating at 300 cycles per minute with a stroke of $2\frac{1}{4}$ inches in a room maintained at 82° F and 45 per cent relative humidity. B. F. Goodrich data are reported as a quality index, which is defined as the ratio of the observed flexures to the flexures of a similar GR-S tread stock having a hysteresis temperature rise equal to the observed hysteresis temperature rise. The relation between flexing and hysteresis temperature rise for a GR-S tread stock compounded with EPC carbon black and for the particular test conditions used here is expressed by the following equation[7]:

$$\log_{10} \text{flexures} = 0.0126\Delta T + 4.28$$

where ΔT is the hysteresis temperature rise above 212° F, as determined using the Goodrich flexometer with a 55-pound load and a $17\frac{1}{2}$ per cent stroke.

The significance of the quality index has been discussed by Juve[7].

At the United States Rubber laboratories, cut growth was measured by flexing a De Mattia bend-flexing specimen, with a circular groove through an 85° arc at 287 cycles per minute. A pin hole is placed in the center of the groove to start cut growth; results are given in kilocycles required for growth of the pin hole to a cut 1 inch long. All results reported are the averages of simultaneous tests on three specimens. Hysteresis measurements were made on the torsional hysterometer[8]. Values for hysteresis are reported as a logarithmic decrement, K, which is proportional to the fractional energy loss per cycle of damped oscillation, when the fractional energy loss per cycle is small.

Low-temperature flexibility.—As a measure of low-temperature flexibility, Young's modulus was determined for the temperature range +30° to −30°C by the method of Green and Loughborough[9]. Brittle points are reported as the highest temperature in ° C at which a 1-inch square, 0.1-inch thick specimen shatters under the impact of a 290-gram weight dropped from a height of 20 inches. The weight is guided during fall through a slot, and the contact end is fitted with a $\frac{1}{4}$-inch movable ball bearing.

RESULTS OF EVALUATION TESTS

Processability: mill compounding and fabrication.—The S-BS copolymers broke down nicely on a cold mill and gave no difficulty in mixing. On a laboratory mill S-BS showed more tackiness than GR-S. However, when

TABLE II

PROCESSABILITY DATA FROM UNITED STATES RUBBER COMPANY LABORATORIES

Code	S-BS I	S-BS II	S-BS IV	GR-S	J-99
Description	Sodium (75:25)	Sodium (75:25)	Sodium (75:25)	Emulsion (75:25)	Emulsion (40:60)
Brittle point (° C)	−24	−24	−30	−65	−12
Initial viscosity (Mooney, large rotor, 4-minute run at 212° F)	79	50	98	45	Slipped
Shrinkage (%)	20.5	6.0	23.0	47	31
Rugosity	0.25	0.13	0.21	0.62	0.14
Carbon black stiffening	—	—	29	35	—
Final viscosity (Mooney, large, rotor, 4-minute run at 212° F)	80	64	—	56	52

TABLE III

STRESS-STRAIN DATA FROM UNITED STATES RUBBER COMPANY LABORATORIES

Polymer code	S-BS III*	S-BS IV†	GR-S	J-99
Description	Sodium (75:25)	Sodium (75:25)	Emulsion (72:28)	Emulsion (40:60)
Brittle point (° C)	−24	−30	−60	−12
Cure (min. at 292° F)	25	30	25	25
Green tensile (lb./sq. in.)	2350	2500	2100	2100
Stress at 300% elong. (lb./sq. in.)	750	800	550	500
Elongation at break (%)	590	560	650	640
Green tensile at 212° F (lb./sq. in.)	1000	1000	770	1100
Elongation at break (%)	410	370	430	760
Aged tensile (aged 48 hr. at 212° F) (lb./sq. in.)	2050	2200	1700	2500
Elongation at break (%)	220	300	200	250
Cure (min. at 292° F)	50	50	50	50
Green tensile (lb./sq. in.)	2000	2500	2700	2700
Stress at 300% elong. (lb./sq. in.)	1200	1450	1050	1300
Elongation at break (%)	400	420	510	460
Green tensile at 212° F (lb./sq. in.)	710	725	940	1500
Elongation at break (%)	260	230	300	510
Aged tensile (aged 48 hr. at 212° F) (lb./sq. in.)	1500	1900	1700	2000
Elongation at break (%)	190	290	180	190
Cure (min. at 292° F)	180	—	180	180
Green tensile (lb./sq. in.)	2050	—	2300	2400
Stress at 300% elong. (lb./sq. in.)	—	—	1700	2100
Elongation at break (%)	280	—	360	320
Green tensile at 212° F (lb./sq. in.)	730	—	990	1300
Elongation at break (%)	180	—	260	270
Aged tensile (aged 48 hr. at 212° F) (lb./sq. in.)	1950	—	2100	2500
Elongation at break (%)	200	—	240	230

* 5.0 parts stearic acid added during compounding.

† 4.0 parts stearic acid added during compounding. Emulsion polymers prepared on soap normally retain 3–5 parts fatty acid.

mixed in an internal mixer maintained at 320° F, the S-BS compound crumbled near the end of the mixing period. S-BS copolymers can be softened by JMH, a proprietary chemical peptizing agent[10].

The results of a typical set of processability tests are given in Table II. These data show S-BS to be equal or superior to GR-S in most processing characteristics. The processing properties of preplasticized S-BS (S-BS II) were outstanding. It is indicated that S-BS can be economically compounded, and that satisfactory calendered and extruded products can be fabricated with less filler than is required for GR-S. The high styrene emulsion polymer J-99 was demonstrated to have essentially the same processing advantages as S-BS.

Stress-strain.—Tables III, IV, and V give test results typical for S-BS and for standard GR-S. Data are also included for two high-styrene emulsion copolymers, so that a comparison of sodium and emulsion copolymers can be made on an equivalent brittle point basis. These data represent S-BS to have stress-strain properties in the same range as GR-S at room temperature, at 212° F, and after accelerated aging tests. However, S-BS vulcanizates retain

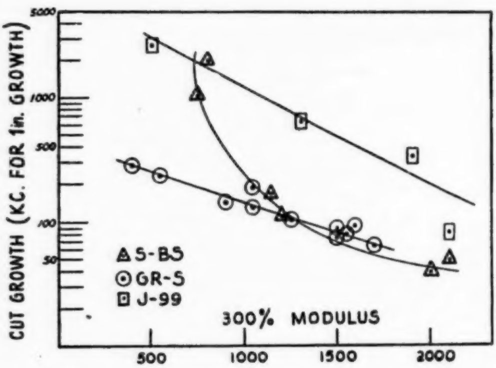

FIG. 1.—Cut growth plotted against modulus.

a higher percentage of their room temperature elongation at 212° F and after accelerated aging than do GR-S vulcanizates. These data indicate an improvement in these properties for S-BS over GR-S.

The testing program was not sufficiently extensive to demonstrate any effect on stress-strain properties of polymerization temperature changes and molecular weight changes over the ranges studied.

Since extensive compounding studies could not be made with the limited amount of material available, no definite conclusions can be arrived at concerning the optimum stress-strain possibilities. However, it is indicated that no exceptional advantages over GR-S are to be expected. In the single test made, the high styrene vulcanizates showed stress-strain properties at 212° F better than those of the control. These values are particularly outstanding, and have seldom been duplicated in GR-S.

Flex crack growth-hysteresis balance.—Figure 1 summarizes the data obtained at the United States Rubber laboratories relating cut growth to modulus. The modulus values reported are stress at 300 per cent elongation measured at room temperature. The data were for different stocks measured at different times; also minor compounding changes were made. The $\log_{10}$ (*KC* for 1-inch growth) is plotted against modulus for convenience. The graph indicates that

TABLE IV

EVALUATION OF SODIUM-CATALYZED 75 BUTADIENE:25 STYRENE COPOLYMERS
(Data from The B. F. Goodrich laboratories)

Identification	Mooney viscosity*	Sulfur (parts)	Cure at 280° F (min.)	300% modulus (lb. per sq. in.)	Tensile (lb. per sq. in.)	Elongation (%)	Hysteresis temp. rise above 212° F (° F)	Flexing	Quality index
30° C S-BS	—	1.75	30	1015	3060	580	49	770,000–8	9.6
			45	1415	2700	425	43	460,000–8	7.2
50° C S-BS	62	2.0	75	960	2400	580	43	550,000–8	8.4
			150	1190	2390	530	37	550,000–8	10.0
GR-S control	47	1.75	75	1020	3380	648	79	690,000–8	3.6
			150	1040	2810	567	58	440,000–8	4.2
Emulsion-polymerized 50 butadiene–50 styrene	54	1.75	75	1200	3900	593	64	1,552,000–8	9.5
			150	1600	4000	527	53	604,000–8	6.8

* Mooney viscosity (at end of a 4-minute run) at 212° F, using the large rotor.

TABLE V

EVALUATION OF 30° C SODIUM-CATALYZED 75 BUTADIENE:25 STYRENE COPOLYMER
(Data from The B. F. Goodrich laboratories)

Property	S-BS untreated		S-BS softened with 1% JMH		S-BS internally mixed at 320° F		GR-S control	
Cure (min. at 280° F)	75	150	75	150	75	120	75	120
Tensile at room temp. (lb./sq. in.)	2375	2375	2025	2425	1600	2050	2200	2350
Elongation at room temp. (%)	575	510	510	500	735	575	615	575
300% modulus at room temp. (lb./sq. in.)	—	—	1000	1250	500	900	800	1050
Tensile at 212° F (lb./sq. in.)	—	—	—	—	—	730	640	—
Elongation at 212° F (%)	—	—	—	—	—	455	420	—
% of elong. retained at 212° F	—	—	—	—	—	79	68	—
300% modulus at 212° F (lb./sq. in.)	—	—	—	—	—	380	330	—
Tensile aged 10 hr. in air bomb (lb./sq. in.)	—	—	—	—	—	1960	1690	—
Elongation, aged 10 hr. in air bomb (%)	—	—	—	—	—	560	430	—
300% modulus, aged 10 hr. in air bomb (lb./sq. in.)	—	—	—	—	—	950	1110	—
% of elong. retained on aging	—	—	—	—	—	97	70	—
Hysteresis temp. rise at 212° F (° F)	71	370	75	58	—	92	119	—
Flexing $\times 10^{-3}$	2000–7*	740–8*	2000–6*	690–8*	990–2*	2000–3*	990–2*	2000–3*
Quality index	13	13.4	11	6.6	—	7.2	2.0	2.2
Permanent set (%)	27.9	12.1	22.8	21.0	—	45.0	—	—
Durometer hardness	—	—	—	—	54	57	55	60
Schopper rebound (%)	—	—	—	—	20	20	34	35
Extrusion plasticity (cc./min.)	—	—	—	—	6.53	—	7.18	—

* First number indicates number of flexures; second number is an arbitrary rating of size of crack at end of flexing period.

the cut growth of S-BS is far superior to that of GR-S at low modulus, but approximately equivalent at high modulus. On the other hand, the high-styrene emulsion copolymer retained its good cut growth properties at high modulus. Hysteresis was measured at room temperature and 280° F. Figure 2 presents results of S-BS, GR-S, and high styrene polymer. Although at room temperature the hysteresis of the S-BS was inferior to GR-S, the more important measurement at 280° F showed the S-BS to be definitely better. The data presented in the graph are the only measurements that were made for high styrene polymers.

The balance between flex crack growth and hysteresis temperature rise above 212° F, as reflected by quality index ratings (Tables IV and V), shows that S-BS is much superior to GR-S in this property. Also, their excellent quality indices are but slightly lowered by heat treatment, chemical softening, or milling of the copolymer.

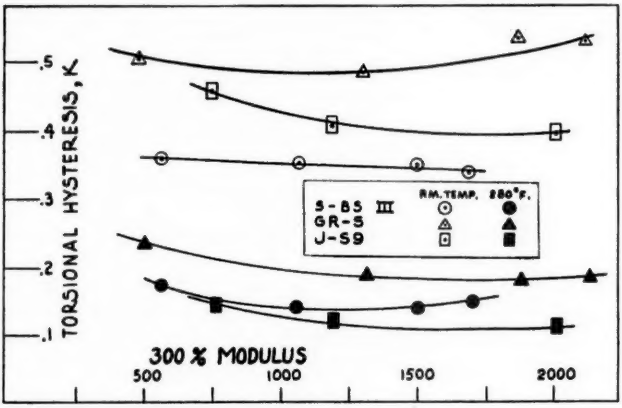

FIG. 2.—Hysteresis plotted against modulus.

These data indicate that S-BS has a flex cracking-hysteresis balance superior to that of GR-S through the whole modulus range. This balance appears to be particularly favorable for low modulus stocks. The good cut growth of the high styrene emulsion polymer allows some compromise in that property in favor of improving hysteresis; the flex cracking–hysteresis balance is indicated to be equal to or better than that of S-BS except for low-modulus, undercured stocks.

Low temperature flexibility.—This property indicates more clearly than any other that a significant difference must exist between the structures of sodium and emulsion polymers of the same butadiene-styrene composition. The S-BS is definitely inferior to GR-S with respect to low temperature flexibility. For a reduction in temperature from +30° to −30° C, an S-BS tread compound increased in Young's modulus from 140 to 20,000 pounds per square inch, whereas a control GR-S compound increased only from 190 to 1300 pounds per square inch (Figure 3). Brittle points of cured S-BS were determined to be −24° and −30° C; a value of −20° C was obtained for raw S-BS. These values compare with −60° and −65° C for tests on cured GR-S. These comparisons are probably typical of butadiene-styrene copolymers prepared by the two methods over a wide range of composition. Emulsion poly-

butadiene was determined to have a brittle point of $-85°$ C for a vulcanized stock, whereas sodium polybutadiene had a brittle point of $-62°$ C for a vulcanized stock and $-50°$ C for a raw stock. The high-styrene emulsion copolymer was prepared with a 40 butadiene: 60 styrene feed, and the brittle point was determined to be $-12°$ C.

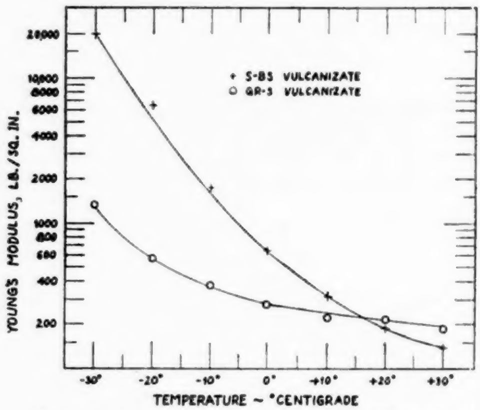

FIG. 3.—Low temperature properties of S-BS and GR-S vulcanizates.

SUMMARY

Sodium-catalyzed butadiene-styrene copolymers (S-BS), of composition 75 weight-per cent butadiene:25 weight-per cent styrene, have been compounded in tread type recipes. Evaluation tests showed properties significantly different from those of GR-S, the emulsion-phase free radical–catalyzed copolymers of identical monomer composition.

1. The processing characteristics of S-BS are considerably superior to those of GR-S, although one experience with a high temperature internal mix may indicate some limitation. Objective laboratory processing tests show that S-BS resembles high-styrene emulsion copolymers in that it can be satisfactorily fabricated from stocks containing less filler than is required in GR-S stocks for similar uses.

2. Stress-strain properties based on limited compounding studies are similar to those of GR-S.

3. The flex crack growth–hysteresis balance for S-BS vulcanizates is much superior to that of GR-S vulcanizates. Vulcanizates of emulsion polymers of high styrene content also had a flex crack growth–hysteresis balance superior to that of GR-S vulcanizates.

4. The low temperature properties of S-BS vulcanizates are inferior to those of GR-S vulcanizates. Brittle points and low temperature Young's modulus of S-BS vulcanizates are much higher than those of GR-S vulcanizates.

REFERENCES

[1] Marvel, Bailey, and Inskeep, *J. Polymer Science* **1**, 275 (1946).
[2] Schultz and Bryant, *J. Applied Physics* **15**, 360 (1944).
[3] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).
[4] White, Ebers, and Shriver, *Ind. Eng. Chem.* **37**, 767 (1945).
[5] Garvey, *Ind. Eng. Chem.* **34**, 1320 (1942).
[6] Lessig, *Ind. Eng. Chem. Anal. Ed.* **9**, 582 (1937).
[7] Juve, *Ind. Eng. Chem.* **39**, 1494 (1947).
[8] Mooney and Gerke, *India Rubber World* **103**, 29 (Jan. 1941).
[9] Greene and Loughborough, *J. Applied Physics* **16**, 3 (1945).
[10] Manufactured by the J. M. Huber Corp., New York.

EFFECTS OF CROSS-LINKING AND BRANCHING ON THE MOLECULAR CONSTITUTION OF DIENE POLYMERS *

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The polymerization of dienes is usually accompanied by cross-linking reactions. While the percentage of the structural units which are cross-linked is almost always too small to be determined by chemical methods, they are frequently sufficient in number to seriously alter some of the physical properties of the polymerization products and to complicate their structural interpretation. Only a very small degree of cross-linking is sufficient to cause formation of a gel fraction which is insoluble in the usual solvents for the particular type of polymer and, hence, is not amenable to ordinary physico-chemical methods of characterization. Even if the number of cross-linkages is insufficient to cause gelation, the molecular-weight distribution may be severely distorted by them. The molecular-weight distribution under these circumstances does not occupy its usual significance, either in reference to the physical characteristics of the product, or to the kinetic mechanism of the primary polymerization reaction.

In the present paper the probable origin of the cross-linkages formed during the polymerization of dienes will be considered, and their effects on the polymer constitution and properties will be analyzed in the light of the statistical theory of three dimensional polymerizations.

I. REACTION MECHANISMS

Cross-linking.—The most likely mechanism for the formation of cross-linkages during polymerization (or copolymerization) of a 1,4-diene consists in the occasional addition of a growing free radical chain to an unsaturated carbon of a previously polymerized diene unit. The process, in the case of butadiene polymerizations, can be represented as shown on top of page 462, where the long dashes indicate continuation of polymer chains. (The number "3" is assigned to these reactions, "1" being reserved in accordance with convention for initiation and "2" for normal propagation with monomer.) Chain growth may continue by successive addition of monomers proceeding from the free radical of one or the other of the above products. The net result of intervention of reaction (3a) or (3b) in the growth process is the introduction of a cross-linkage between the polymer chain which is in the process of growth and another which was formed at an earlier stage of the conversion of monomer to polymer.

Often the view is expressed that diene polymer, or copolymer, molecules are highly ramified, irregular structures composed of relatively short chains joined together at numerous cross-linkages and (or) branch points. While this view possibly may be correct in some cases, it should be recognized that

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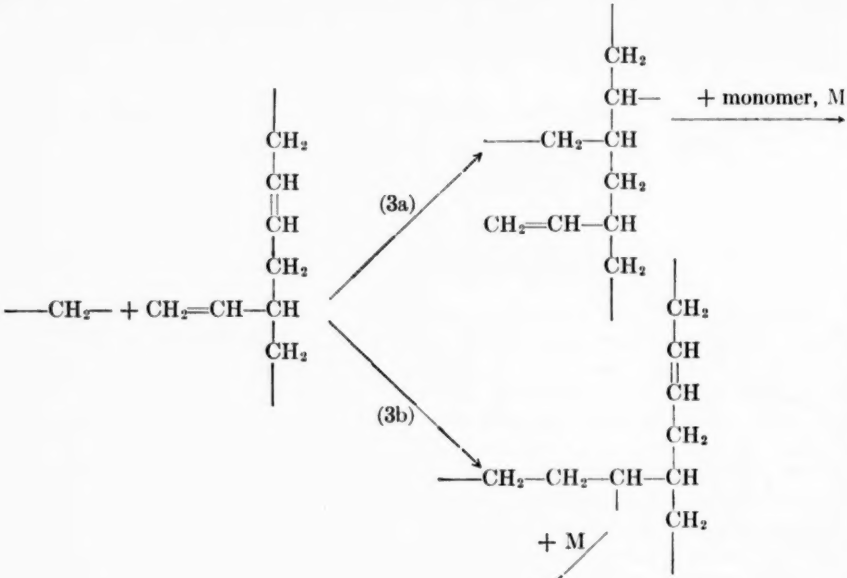
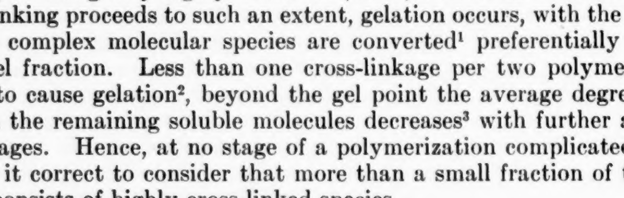


cross-linking reactions, such as the ones shown above, are incapable in themselves of producing very highly branched (finite) molecules. Before the degree of cross-linking proceeds to such an extent, gelation occurs, with the result that the more complex molecular species are converted[1] preferentially to the insoluble gel fraction. Less than one cross-linkage per two polymer chains is required to cause gelation[2], beyond the gel point the average degree of cross-linking in the remaining soluble molecules decreases[3] with further addition of cross-linkages. Hence, at no stage of a polymerization complicated by cross-linking is it correct to consider that more than a small fraction of the soluble polymer consists of highly cross-linked species.

Branching.—On the other hand, chain branching may occur during polymerization as a result of chain transfer between the free radical terminus of a growing chain and a previously formed polymer molecule[4], as shown in formulas below. Subsequent growth from the substituted allyl radical[5] of the polymer chain gives rise to a branch in the structural pattern of the molecule. Branching reactions of this sort cannot cause gelation without the assistance of other inter-linking processes. If transfer occurs readily and the reaction is carried to high conversions, highly branched molecules may be formed, and the molecular size distribution may be considerably distorted, but branching by transfer alone does not produce infinite networks[6]. This branching mechanism may occur in the polymerization of vinyl monomers as well.



In the present paper we are primarily concerned with cross-linking processes, although a few remarks occurring toward the end of the Discussion pertain to the probable influence of branching on physical properties.

II. KINETIC TREATMENT OF CROSS-LINKING REACTIONS

Dependence of degree of cross-linking on conversion.—The rate of conversion of monomer to polymer can be written in the usual form:

$$d\alpha/dt = k_2[R^*](1 - \alpha) \qquad (1)$$

where α is the fractional extent of conversion of monomer to polymer, k_2 is the velocity constant for normal chain propagation, and $[R^*]$ represents the concentration of free radicals. The rate[7] at which cross-linkages are formed by propagation steps in which a previously polymerized unit is involved in accordance with reactions (3a) or (3b) is given by $k_3[R^*]\alpha$. It is convenient to consider that a diolefin monomer which eventually becomes cross-linked contributes two structural units, one to each of two "primary molecules". The term "primary molecule"[8] has been applied to designate the linear molecules which would exist if all cross-linkages were severed. The same meaning is intended here, although it is difficult to visualize severance of the cross-linkage formed in reaction (3a) without also rupturing a primary molecule. For present purposes the primary molecules may be defined as the molecules which would exist if cross-linking additions (3a) and (3b) had been omitted from the growth processes. Throughout this paper it is assumed that no more than a very small fraction of the structural units become involved in cross-linkages.

If ν is chosen to represent the proportion of cross-linked units (expressed as moles of cross-linked units per mole of monomer initially present), then in the light of the above definitions:

$$d\nu/dt = 2k_3[R^*]\alpha \qquad (2)$$

Dividing Equation (2) by (1):

$$d\nu/d\alpha = 2K\alpha/(1 - \alpha) \qquad (3)$$

where $K = k_3/k_2$ is the "reactivity ratio"[9] of an unsaturated polymer unit as compared with a monomer molecule. Integrating Equation (3) and dividing ν by α to obtain the "density" ρ of cross-linked units in the polymerized portion of the mixture:

$$\rho = (\nu/\alpha) = -2K[1 + (1/\alpha)\ln(1 - \alpha)] \qquad (4)$$

This function, plotted in Figure 1, increases rapidly as α approaches unity. In other words, the density of cross-linkages increases markedly at higher conversions. Suppression of gelation is known to become increasingly difficult with increase in conversion, as would be expected from the curve in Figure 1 and the considerations leading to its derivation.

To illustrate more fully the significance of Figure 1, suppose that in a given diene polymerization the relative reactivity ratio $K = k_3/k_2$ is equal to 5×10^{-4}. The ordinates in Figure 1 correspond then to $\rho \times 10^3$. According to statistical theory[10], neglecting the effects of departure from randomness in the distribution of cross-linked units (*cf. seq.*), gelation occurs when ρ exceeds the reciprocal of the weight average degree of polymerization of the primary molecules, *i.e.*, the weight average degree of polymerization which would prevail if no cross-

linkages had been formed. If, for example, the weight average primary chain length is 5000 units, gelation should occur (see Figure 1) at about 32 per cent conversion[11]; if it is 2000 units, the polymerization should proceed to 57 per cent conversion before gel is formed; and for a weight average of 1000 units per primary molecule, gelation should occur at 80 per cent conversion. The accelerated rise of the curve of Figure 1 at higher conversions indicates that, to further postpone gelation, the average size of the primary molecules must be suppressed more drastically.

Conversely, the above calculations could be employed to compute the constant K from the percentage conversion at the gel point and the weight average degree of polymerization, $\bar{y}_w$, of the primary molecules. In the GR-S polymerization, for example, gelation occurs at about 70 per cent conversion under conditions (modifier concentration) such that $\bar{y}_w$ can be estimated to be of the order of 1000 to 2000 units. At 70 per cent conversion $\rho/2K$ is about 0.7. Taking $\rho = 1/\bar{y}_w$ at the gel point, K is of the order of 5×10^{-4} [12].

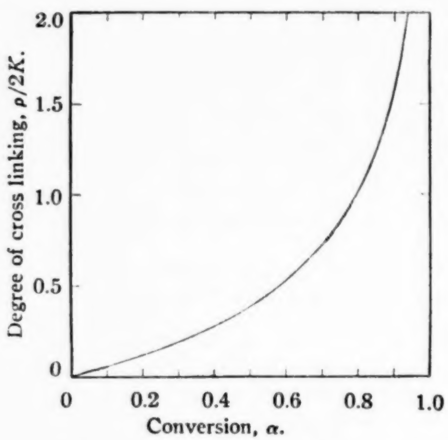


FIG. 1.—Degree of cross-linking expressed in arbitrary units ($\rho/2K$) *vs.* conversion calculated from Equation (4), based on the cross-linking mechanism shown in reactions (3a) and (3b)

In making these calculations relating to the gel point, the distribution in primary molecular sizes is unimportant provided the weight average is taken. If, for example, the average chain length of molecules formed at conversion α decreases with α (or if it increases with α owing to depletion of modifier), it is necessary only to compute the weight average size for all primary molecules. If cross-linking is excessively nonrandom (*cf. seq.*), this generalization will require modification.

The action of "regulators", or "modifiers", *e.g.*, thiols[13], in postponing the occurrence of gelation to higher conversions is in harmony with the above treatment. Functioning as a chain transfer agent[14], the regulator merely reduces the average primary molecular weight. This suppression of gelation with attendant improvement in processibility is accomplished, however, only at the sacrifice of other desirable properties as will be pointed out in a later section of this paper. There is no reason to believe that the regulator, or any other added substance, actually suppresses cross-linking reactions, nor is there justification for the frequent assertion that the regulator gives rise to a more linear polymer,

except in the sense that there are fewer cross-linkages per molecule owing merely to the smaller sizes of the molecules.

According to the above mechanism, cross-linking proceeds simultaneously with the polymerization at a relative rate dependent only on the relative concentrations of polymer and monomer, and on the characteristic relative reactivity ratio, K, for polymer units as compared with monomer. In general, K depends on temperature, but is independent of the catalyst, activators, etc., so long as the polymerization is propagated by free radicals.

Nonrandomness in the distribution of cross-linked units.—Theories of molecular-weight distribution and gelation in three dimensional polymers invariably have employed the assumption that the cross-linkages occur at random, *i.e.*, that the probability that any given structural unit bears a cross-linkage is independent of the status of other units in the same chain or molecule. This assumption is not strictly valid in polymers cross-linked during polymerization by a mechanism such as the one presented above. Proof for this statement can be set forth as follows.

Consider primary molecules, growth of which occurred during a brief interval at the conversion α'. A fraction ρ_i of their structural units will have been formed by reactions (3a) or (3b) from members of previously polymerized molecules; *i.e.*, a fraction $\bar{y}_i$ of the units of the primary polymer molecules formed at conversion α' will be cross-linked immediately on polymerization. As the conversion proceeds from α' to α, an additional fraction ρ_a of the structural units of these same primary molecules will become involved in cross-linkages with subsequently formed primary molecules. The fraction of cross-linked units at conversion α in primary molecules which were formed at conversion α' is:

$$\rho_{\alpha'} = \rho_i + \rho_a$$

Both ρ_i and ρ_a are assumed to be very small compared with unity.

The quantity ρ_i is simply equal to the ratio of the rate of generation of cross-linkages $(d\nu/2dt)$ to the rate of polymerization at conversion α':

$$\rho_i = (d\nu/2d\alpha)_{\alpha'} = K\alpha'/(1 - \alpha') \tag{5}$$

The rate at which additional cross-linked units are acquired by these same primary molecules is

$$n_{\alpha'} d\rho_a/dt = k_3 n_{\alpha'}[R^*]$$

where $n_{\alpha'}$ is the number of structural units polymerized within an interval at α'. Dividing by Equation (1):

$$d\rho_a/d\alpha = K/(1 - \alpha) \tag{6}$$

$$\rho_a = K \int_{\alpha'}^{\alpha} d\alpha/(1 - \alpha) = K \ln\left(\frac{1 - \alpha'}{1 - \alpha}\right) \tag{7}$$

Hence

$$\rho_{\alpha'} = K\left[\alpha'/(1 - \alpha') + \ln\left(\frac{1 - \alpha'}{1 - \alpha}\right)\right] \tag{8}$$

Equation (8) gives the degree of cross-linking occurring in primary molecules formed at conversion α' after the polymerization has been continued to conversion $\alpha > \alpha'$. According to Equation (8) primary molecules formed at higher conversions carry a greater proportion of cross-linked units than those formed earlier. It is obvious that the number of cross-linked units at the in-

stant of formation should be fewer at lower conversions, but it would not necessarily have been self-evident that subsequent cross-linking of some of the units of these molecules fail to make up this deficiency.

Under these circumstances it is not permissible to assume that the probability that a given structural unit is cross-linked is entirely independent of the status of other units of the same primary molecule. Probabilities for the occurrence of cross-linked units differ for different primary molecules. If an abnormally large fraction of some of the units in a given primary molecule are found to be cross-linked, it is likely that this molecule was formed during the latter range of the conversion of monomer to polymer; hence, a higher than average probability ρ is likely to apply to other units in this molecule.

For the purpose of exploring the magnitude of this variation in ρ for polymer chains formed at different stages of the polymerization, it is instructive to examine the ratio of ρ_α, the degree of cross-linking in primary molecules formed at the final conversion α, to ρ_0, the degree of cross-linking in the coexisting primary molecules which were formed at the outset of the polymerization. Setting α' successively equal to α and to 0 in Equation (8) and dividing:

$$\rho_\alpha/\rho_0 = \frac{-\alpha}{(1-\alpha)\ln(1-\alpha)} \tag{9}$$

In Figure 2 this function is plotted against α. Only at high conversions does the spread between the average degree of cross-linking become significantly

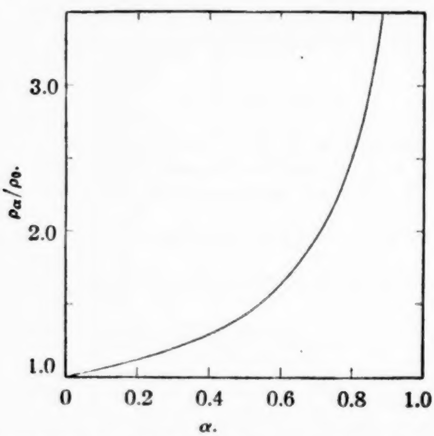


FIG. 2.—Nonrandom distribution of cross-linkages *vs.* conversion. The ratio of cross-linked units in primary molecules formed, respectively, at conversions α and 0 *vs.* conversion α Curve computed from Equation (9).

large, as indicated by the ratio greater than unity. It is the extreme variation in average degrees of cross-linking which is indicated here, the mean deviation being considerably smaller. For ordinary purposes, disregard of the departure from random cross-linking probably can be ignored up to 60 or 70 per cent conversion. At higher conversions the variation may be large enough to upset precise calculation of gel points, sol-to-gel conversion, etc.[15]. Gelation should occur at a somewhat lower degree of cross-linking than would be the case if the cross-linked units were distributed among the various primary molecules at random.

Change in number of polymer molecules with conversion.—Wall and Beste[16] have deduced from osmotically determined molecular weights of samples of emulsion copolymers of butadiene and styrene (GR-S) removed at intervals that at high conversions approaching the point at which gel makes its appearance the total number of polymer molecules actually decreases with conversion. In other words, cross-linking reactions decrease the number of molecules faster than new ones are generated at higher conversions. It is of interest, therefore, to determine whether or not the mechanism of cross-linking employed here is consistent with this observation.

The number of cross-linkages formed per unit polymerized is $d\nu/2d\alpha$ and the corresponding rate of generation of primary molecules ($dN/d\alpha$) is $1/\bar{y}_{n,\alpha}$ where $\bar{y}_{n,\alpha}$ is the number average number of units per primary molecule formed at conversion α. If intramolecular cross-linkages are neglected (the present deductions being limited to conversions preceding gelation), then the rate of change in the total number of molecules is equal to the latter quantity minus the former. It is convenient to take the ratio of these two quantities:

$$2dN/d\nu = (1/\bar{y}_{n,\alpha})(2d\alpha/d\nu) = (1 - \alpha)/\alpha K\bar{y}_{n,\alpha} \tag{10}$$

as an index, which is less than unity when the total number of polymer molecules is decreasing with conversion.

For the purpose of illustrating the significance of Equation (10), we may inquire under what conditions $2dN/d\nu$ becomes less than unity at conversions up to the gel point. According to the statistical theory of network formation[17], $\rho = 1/\bar{y}_w$ at the gel point, where $\bar{y}_w$ is the weight average molecular weight of primary molecules (not merely those formed at conversion α), neglecting, of course, the minor effects of nonrandom distribution of cross-linkages. Hence, according to Equation (4):

$$\tfrac{1}{2}K\bar{y}_w = -\left[1 + (1/\alpha_c)\ln(1 - \alpha_c)\right]$$

where α_c is the critical value of the conversion for incipient gelation. Employing this relationship to eliminate the parameter K from Equation (10), there is obtained for the ratio of rate of formation of new chains to rate of combination with those formed previously:

$$2dN/d\nu = -\{[(1 - \alpha_c)/\alpha_c][2 + (2/\alpha_c)\ln(1 - \alpha_c)]\}\bar{y}_w/\bar{y}_{n,\alpha} \tag{11}$$

The quantity in braces in Equation (11) decreases from unity to zero as α_c goes from zero to unity; it reaches the value $\frac{1}{2}$ near $\alpha_c = 0.80$. If the ratio of chain transfer agent to monomer is constant throughout the polymerization, then $\bar{y}_{n,\alpha}$ is independent of α and equal to the over-all $\bar{y}_n$. Under these circumstances $\bar{y}_w$ is twice $\bar{y}_n$. Hence, $2dN/d\nu$ exceeds unity up to the gel point, provided gelation occurs at $\alpha < 0.80$; if gelation occurs at $\alpha > 0.80$ this ratio is less than unity at the gel point, corresponding to a net decrease in the number of polymer molecules.

In the thiol regulated copolymerization of butadiene and styrene, the regulator usually is consumed relatively more rapidly than the monomers[18]. Hence, $\bar{y}_{n,\alpha}$ exceeds $\bar{y}_w/2$, and, consequently, $2dN/d\nu$ may fall below unity before gelation occurs at conversions somewhat less than 80 per cent. Thus, the mechanism of cross-linking proposed here is consistent with the observations of Wall and Beste.

III. PHYSICAL PROPERTIES IN RELATION TO STRUCTURE

Physical properties of high polymers necessarily are dependent on molecular weight and molecular-weight distribution. In diene polymers and copolymers containing occasional cross-linkages, however, the actual connection between physical properties and molecular weight is especially elusive owing to disturbing variations in molecular pattern and to peculiarities of the molecular-weight distribution caused by the cross-linkages.

The molecular-weight distribution, according to theory[17], is broadened by the introduction of cross-linkages. This broadening becomes extreme as the gel point is approached. Experimental determination of the molecular-weight distribution in partially cross-linked polymers is difficult[19]. The usual fractionation methods based on solubility differences can be expected at best to be only of limited value inasmuch as two polymer molecules of the same molecular weight, one of them composed of several primary molecule chains and the other of a single linear chain, may differ significantly in solubility. Hence, separations do not take place explicitly according to molecular weight.

Even if the molecular-weight distribution were accurately determinable by fractionation or any other method, physical properties of the polymer generally could not be predicted unambiguously without also taking into account the concentration of cross-linkages. Properties of vulcanized rubberlike diene polymers are of particular interest in this connection.

The structure of the vulcanized rubber is adequately described as a network composed of primary molecules of given molecular weight and molecular-weight distribution randomly inter-linked by cross-linkages (or interunit linkages of higher functionality in some cases). A small fraction of these cross-linkages may have been formed before the vulcanization operation, but from the standpoint of vulcanizate structure (and properties) it is unimportant to differentiate between those formed prior to and those formed during vulcanization; only the total number of cross-linkages is significant. Similarly, the molecular-weight distribution before vulcanization is unsuitable as a basis of correlation when cross-linkages are present and should be discarded in favor of the primary molecular-weight distribution, *i.e.*, the molecular-weight distribution in the total absence of cross-linkages. It has been possible to account quantitatively in terms of structure for various physical properties of Butyl rubber by proceeding from this point of view[20]. Although unvulcanized Butyl rubber is essentially free of cross-linkages, there is no basic reason for doubt that this same scheme also can be applied successfully to other vulcanized rubbers[21].

The regulator, or modifier, by reducing the primary molecular weight prevents gelation, or suppresses it sufficiently, so that the resulting polymer retains thermoplasticity to the degree necessary for processing. This result is achieved, however, only at a sacrifice in the perfection of the network structure formed during vulcanization. As shown previously[22], each end of a primary molecule contributes a flaw to the vulcanizate structure. The number of these flaws, or "terminal chains" which are not subject to permanent orientation when the vulcanizate is deformed, is inversely proportional to the number average molecular weight of the primary molecules; consequently, the number of flaws in the vulcanizate network increases directly with the amount of modifier consumed during polymerization. Modulus, creep and tensile strength are influenced by the abundance of these flaws in the network structure[20]. A deficiency in modulus may, of course, be compensated by increasing the degree of cross-linking, but the loss in strength, and presumably in related

physical properties as well, cannot be overcome in this manner. Thus, circumvention of the processing difficulties precipitated by cross-linking reactions through suppression of the primary molecular weight with a regulator can be expected to be accompanied to some extent by impairment of physical properties.

The determination of the primary molecular-weight distribution, as required for interpretation of the properties of network structures produced by vulcanization, may be difficult in a polymer containing cross-linkages. It may be deduced, however, from detailed knowledge of the reaction kinetics. If, for example, the transfer constant[16] for the regulator is known, the primary molecular-weight distribution may be computed.

The number average primary molecular weight, without regard for the distribution, usually suffices for characterizing the properties of a network structure. If a fragment of the transfer agent combines with each primary molecule, the number average primary molecular weight may be secured by analytical determination of this fragment. Alternatively, an approximate value may be obtained from osmotic measurements applied to the nongelled polymer. According to theory[3], the number average molecular weight is altered relatively little by cross-linking up to the point at which gel appears. The number average primary molecular weight therefore does not differ seriously from the observed osmotic value for the cross-linked polymer.

Thus far the discussion has been concerned with the effects of cross-linking on linear polymer molecules. It has been suggested frequently that diene synthetic rubber molecules are highly branched, although no conclusive data bearing on this point are available. As already noted a preponderance of highly branched molecules cannot be produced by cross-linking reactions alone, owing to the intervention of gelation. However, branching reactions such as the one depicted in reaction (4) may conceivably result in highly branched polymer molecules. It may be of interest, therefore, to consider briefly some of the characteristics to be expected in network structures formed by cross-linking branched molecules.

For a given molecular-weight distribution, the same member of cross-linkages introduced at random gives rise to the same number of active network elements[22], regardless of whether the molecules are linear or branched (or cross-linked). Hence, elastic modulus should not be affected very much by branching. On the other hand, a network formed from branched molecules has many more terminal chains[22]; consequently a larger proportion of the structure is not oriented by stretching. On this basis a vulcanizate formed from branched molecules could be expected to exhibit lower strength than one formed from linear molecules of the same molecular weight. It is important, therefore, to distinguish branching from cross-linking reactions.

SUMMARY

Reaction mechanisms whereby cross-linked and branched polymer structures may be formed during the polymerization of dienes are discussed. A kinetic treatment of the formation of cross-linkages *via* the occasional addition of a free radical to the unsaturated carbon of a structural unit of a previously polymerized molecule is presented. It is pointed out that the rate of this addition step relative to monomer addition can be deduced from the average chain length and the conversion at which gelation occurs.

Cross-linkages introduced by the mechanism under consideration are not distributed at random, but the deviations from a random distribution are

unimportant except at high conversions. Conditions are examined under which the cross-linking reaction decreases the total number of molecules more rapidly than they are formed.

Physical properties of polymers (with particular emphasis on vulcanized rubbers) are most conveniently interpreted in terms of (1) the primary molecular weight (*i.e.*, molecular weight in the absence of cross-linkages) and its distribution, and (2) the concentration of cross-linkages. The actual molecular-weight distribution, which may be severely distorted by the presence of cross-linkages, is inappropriate for direct correlation with the more important physical properties. The modifiers or regulators commonly employed in diene polymerizations suppress gel formation by reducing the primary molecular weight; they do not actually reduce cross-linking. This reduction in molecular weight is not without other undesired consequences, however.

REFERENCES

[1] Flory, *J. Am. Chem. Soc.* **63**, 3083, 3096 (1941); *J. Phys. Chem.* **46**, 132 (1942).

[2] Stockmayer, *J. Chem. Physics* **12**, 125 (1944); Flory, *J. Am. Chem. Soc.* **69**, 30 (1947).

[3] Flory, *J. Am. Chem. Soc.* **63**, 3083, 3096 (1941); **69**, 30 (1947); *J. Phys. Chem.* **46**, 132 (1942).

[4] Flory, *J. Am. Chem. Soc.* **59**, 241 (1937).

[5] Bartlett and Altshul (*J. Am. Chem. Soc.* **67**, 812, 816 (1945)) have shown that allyl radicals are relatively unreactive toward allyl acetate or allyl chloride. Instead of starting new chains, the allyl radicals disappear by combination in pairs. The diene monomers (M) are considerably more reactive than the allyl monomers and, further, the concentration of free radicals probably is much lower than in the polymerization of the allylic compounds. Hence, addition of diene monomers may supersede radical combination in the scheme above.

[6] If chain transfer to previously formed molecules occurs with ease so that, in general, each molecule is repeatedly reactivated by transfer, a condition is approached in which each initially formed polymer molecule undergoes further growth at a rate (or with a probability) proportional to its size. Very large polymer molecules could be formed in this manner. The kinetic treatment of this interesting situation has not been included here.

[7] The rate constant k_3 is the mean of K_{3a} and k_{3b} weighted according to the proportions of 1,2 and 1,4 units. Inasmuch as this proportion ordinarily does not vary with conversion, it is permissible to employ k_3 as a constant.

[8] Flory, *Chem. Rev.* **35**, 51 (1944); *J. Am. Chem. Soc.* **69**, 30 (1947).

[9] The quantity K corresponds to $1/\sigma$ in the copolymerization theory of Mayo and Lewis (*J. Am. Chem. Soc.* **66**, 1594 (1944)), to α in the similar theory of Alfrey and Goldfinger (*J. Chem. Physics* **12**, 205 (1944)) and to $1/\gamma_1$ in the terminology adopted recently by Alfrey, Mayo and Wall (*J. Polymer Sci.* **1**, 581 (1946)).

[10] Stockmayer, *J. Chem. Physics* **12**, 125 (1944).

[11] Under conditions such that gelation occurs at lower conversions, calculation of the gel point in this manner is likely to be seriously in error, for reasons pointed out by Walling (*J. Am. Chem. Soc.* **67**, 441 (1945)). It is assumed also, as previously mentioned, that intramolecular connections may be neglected.

[12] Alfrey and Harrison (*J. Am. Chem. Soc.* **68**, 299 (1946)), in an investigation of the copolymerization of allyl chloride with styrene at 70° C, found that the allylic monomer added at a rate only 3 per cent of that for styrene. Reaction (3b), which probably is more rapid than (3a), is an analogous addition of a free radical to a substituted allyl radical. The reactivity ratio K governing the frequency of occurrence of the cross-linking addition reaction is much smaller than 0.03, but the hundredfold difference probably can be attributed to two factors: the small proportion of 1,2-diene units (about 10 to 20 per cent; see Rabjohn, Bryan, Inskeep, Johnston, and Lawson, *J. Am. Chem. Soc.* **69**, 314 (1947)), and the absence of an activating group or atom such as the chlorine in allyl chloride.

[13] Ewart, R. H., private communication to the Office of Rubber Reserve, Dec. 1942; Snyder, Stewart, Allen and Dearborn, *J. Am. Chem. Soc.* **68**, 1422 (1946); Wall, Banes, and Sands, *J. Am. Chem. Soc.* **68**, 1429 (1946); Smith, *J. Am. Chem. Soc.* **68**, 2059, 2064, 2069 (1946).

[14] Flory, *J. Am. Chem. Soc.* **59**, 241 (1937); Mayo, *J. Am. Chem. Soc.* **65**, 2324 (1943).

[15] Flory, *J. Am. Chem. Soc.* **69**, 30 (1947).

[16] Wall and Beste, *J. Am. Chem. Soc.* **69**, 1761 (1947).

[17] Flory, *J. Am. Chem. Soc.* **63**, 3083, 3096 (1941); **69**, 30 (1947); *J. Phys. Chem.* **46**, 132 (1942); Stockmayer, *J. Chem. Physics* **12**, 125 (1944).

[18] Smith, *J. Am. Chem. Soc.* **68**, 2059, 2064, 2069 (1946).

[19] Valyi, Janssen, and Mark (*J. Phys. Chem.* **49**, 461 (1945)) fractionated copolymers of styrene with small percentages of divinylbenzene in an effort to observe effects of cross-linking on molecular-weight distribution. The solutions which they employed probably were too concentrated for efficient separations, and insufficient numbers of fractions were obtained from which to construct significant molecular-weight distribution curves. Their application of molecular-size distribution equations, derived for polymers composed of units of identical functionality, to such systems does not appear to be justified.

[20] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).

[21] The relationship between tensile strength and network structure of the noncrystalline diene rubbers may differ from that for Butyl rubber (*cf.* Flory, *Ind. Eng. Chem.* **38**, 417 (1946)), since the strength of the latter is intimately associated with its ability to crystallize when stretched. Relationships between elastic properties, swelling, and rate of relaxation under stress, on the other hand, should be similar to those which apply to Butyl rubber.

[22] Flory, *Chem. Rev.* **35**, 51 (1944); *Ind. Eng. Chem.* **38**, 417 (1946).

THE ADDITION OF THIO COMPOUNDS TO OLEFINS. II. REACTIONS OF THIOLACETIC AND MONO-, DI-, AND TRICHLOROTHIOLACETIC ACIDS *

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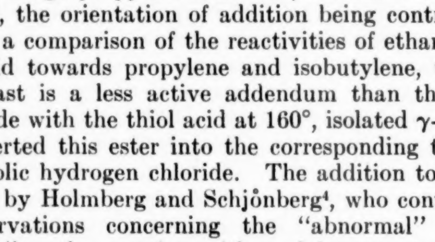
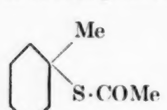
Since thiol acids are a limited group, it is not surprising that their additive reactivity: $>C{:}C< + R{\cdot}CO{\cdot}SH \longrightarrow >CH{\cdot}\overset{|}{C}{\cdot}S{\cdot}COR$, has been but meagrely explored; in fact, the few such reactions reported have been concerned only with thiolacetic acid. Holmberg[1] provided the first example in the preparation of β-phenylethylthiolacetate from styrene in good yield at room temperature. Ipatieff and Friedmann[2] studied the addition to propylene, isobutylene, isopropylethylene, and trimethylethylene at various temperatures and found that, although propylene was inert, the other olefins gave thiolacetates in high yield, the orientation of addition being contrary to Markownikoff's rule. From a comparison of the reactivities of ethanethiol, thiophenol, and thiolacetic acid towards propylene and isobutylene, these authors concluded that the last is a less active addendum than the thiols. Sjöberg[3] treated allyl chloride with the thiol acid at 160°, isolated γ-chloropropyl thiolacetate, and converted this ester into the corresponding thiol by hydrolysis with methyl-alcoholic hydrogen chloride. The addition to some unsaturated acids was followed by Holmberg and Schjånberg[4], who confirmed Ipatieff and Friedmann's observations concerning the "abnormal" orientation. The present work describes the reaction with cyclohexene, 1-methylcyclohexene, dihydromyrcene, squalene, and rubber of thiolacetic and mono-, di-, and trichlorothiolacetic acids, the last two acids being specially synthesized.

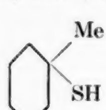
Reactions with thiolacetic acid.—On mixing this acid with the liquid olefins named above, a violent reaction occurred, with the evolution of much heat. The cyclohexene reaction product, isolated by distillation at reduced pressure, was characterized as *cyclohexyl thiolacetate* (I) in the following way. Alkaline hydrolysis gave the thiol (II), whose sodium salt reacted with iodobenzene and with bromoacetic acid to give cyclohexylphenyl sulfide (III) and cyclohexylthioglycolic acid (IV), respectively, which are readily identified by means of

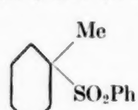


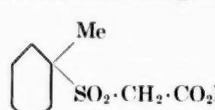
* Reprinted from the *Journal of the Chemical Society*, **1947**, pages 134–141.

their crystalline sulfones[5]. 1-Methylcyclohexene gave an analogous *product*, which could be either the normal (V) or the abnormal (VI, R = Me) ester. Again, the product was hydrolyzed to the *thiol* (VII or VIII), and this was converted into the corresponding phenyl sulfide and thioglycolic acid, which were oxidized to the respective crystalline sulfones, m. p. 108° and 96°. The alternative compounds, (IX) and (X) or (XI) and (XII), have been unambiguously


(V)

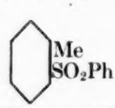

(VII)

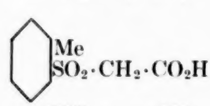

(IX, m. p. 76°)


(X, m. p. 85°)


(VI)


(VIII)


(XI, m. p. 108°)


(XII, m. p. 96°)

differentiated[5], so that m. p. and mixed m. p. data establish with certainty that the sulfones now obtained are (XI) and (XII), and thus that the original ester is (VI, R = Me).

Dihydromyrcene gave two liquid *thiolacetates* corresponding to the mono- and diaddition compounds (XIII and XIV, R = Me), the latter being readily hydrolyzed with alcoholic alkali to the *dithiol* (XV). The squalene reaction *product* when freed from excess of thiol acid in a high vacuum was a colorless

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHMe\cdot S\cdot COR \quad (XIII)$$
$$CHMe_2\cdot CH(S\cdot COR)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHMe\cdot S\cdot COR \quad (XIV)$$
$$CHMe_2\cdot CH(SH)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHMe\cdot SH \quad (XV)$$

viscous oil in which 36 per cent of the double bonds had reacted. The reaction between rubber and the thiol acid was investigated in benzene solution. On irradiating such a solution contained in Pyrex vessels with a mercury-vapor lamp for a few hours and precipitating the *product* with excess alcohol, a white rubberlike material was obtained, in which almost quantitative addition of the thiol acid fragments to the double bonds of the rubber had occurred. The irradiation conditions described appear to be essential for ease of reaction. Illumination with a tungsten-filament lamp, heating the reactants to 100–130° in a Carius tube, and leaving a benzene solution in the light of the laboratory for as long as 2 years, in the presence or absence of ascaridole in each case, only induced a fractional amount of the thiol acid to combine. Irradiation with a carbon arc was more successful, but still considerably less efficient than the mercury-vapor lamp. The almost fully saturated rubber derivatives physically resembled the original rubber, and gave no detectable indications of cross-linking or molecular degradation. Just as with the simpler olefin analogs, the *rubber thiolacetate* could be hydrolyzed to a *thiol*, isolated as a hard fibrous substance. It seems certain that the reac-

$$\cdot CH_2\cdot CHMe\cdot CH(S\cdot COR)\cdot CH_2\cdot \quad (XVI)$$
$$\cdot CH_2\cdot CHMe\cdot CH(SH)\cdot CH_2\cdot \quad (XVII)$$

tion proceeds similarly with all the olefins considered, and therefore that (XVI, R = Me) represents the repeating unit in rubber thiolacetate and (XVII)

that in *rubber thiol*, a decision which is confirmed by ultraviolet absorption measurements.

Reactions with monochlorothiolacetic acid.—When the vigorous reactions of the parent acid with the liquid olefins were repeated with this acid, colorless liquid addition products were obtained in almost quantitative yield. A novel feature of this series, however, is that alkaline hydrolysis of the chlorothiolacetate produces not thiols, but substituted thioglycolic acids; *e.g.*, *cyclohexyl chlorothiolacetate* gives cyclohexylthioglycolic acid, obviously owing to interaction between the thiol and chloroacetic acid, the primary hydrolysis products: $C_6H_{11}\cdot S\cdot CO\cdot CH_2Cl(C_6H_{11}\cdot SH + CH_2Cl\cdot CO_2H) \longrightarrow C_6H_{11}\cdot S\cdot CH_2\cdot CO_2H$. Oxidation of the derived *thioglycolic acid* to its crystalline *sulfone* of known constitution[5] serves to identify the mode of addition to the unsymmetrical olefinic center in 1-methylcyclohexene, and proves that addition proceeds abnormally to give the *ester* (VI, R = CH_2Cl). Dihydromyrcene again gave *mono-* and *diadducts* (XIII and XIV, R = CH_2Cl), the former separable as a pure compound, but squalene, although reacting vigorously, yielded incompletely saturated products.

In marked contrast to thiolacetic acid, monochlorothiolacetic acid reacts readily with rubber in benzene solution in the presence of ascaridole in the dark. Irradiation with the mercury-vapor lamp accelerates the reaction considerably but, even so, the most convenient preparative method is to leave a solution as intimated above in ordinary daylight for a few days and then to precipitate the rubber derivative either with excess of alcohol or following removal of the benzene by steam distillation. The nature of the peroxide catalyst is somewhat critical. Without added peroxide the reaction is extremely slow; benzoyl peroxide is an almost ineffective promoter, *tert*-butyl hydroperoxide is much better, but not nearly so good as ascaridole. By limiting the extent of addition, a whole series of rubber chlorothiolacetates can be obtained, which vary from slightly modified rubber to the almost fully saturated hard solid. From the point of view of possible commercial value, the most interesting derivatives were those in which about three-quarters of the double bonds had been saturated: they possess elastic properties comparable with those of the original rubber, are thermally stable at 140°, and have high resistance to solvents, such as light petroleum (absorption practically nil) and aviation fuel (absorption 20–30 per cent for a fuel containing 35 per cent of aromatic hydrocarbons). The nature of the reaction and the properties of the products leave no doubt that monochlorothiolacetic acid adds to rubber to give an essentially linear polymer with a repeating unit (XVI, R = CH_2Cl), and spectrographic data can again be adduced to confirm this view.

Reactions with dichlorothiolacetic acid.—Addition to cyclohexene, dihydromyrcene, and squalene occurred with the usual facility. *Cyclohexyl dichlorothiolacetate*, $C_6H_{11}\cdot S\cdot CO\cdot CHCl_2$, failed to yield a thiol on hydrolysis, the product being a high-boiling viscous liquid of indefinite constitution, but almost certainly a mixture of α-chlorocyclohexylthioglycolic acid, $C_6H_{11}\cdot S\cdot CHCl\cdot CO_2H$, and biscyclohexylthioacetic acid, $CH(C_6H_{11}S)_2\cdot CO_2H$, which would result from interaction of the initially formed thiol and dichloroacetic acid. Dihydromyrcene gave *mono-* and *diadducts* again (XIII and XIV, R = $CHCl_2$), of which only the former could be fully purified by distillation. From squalene was obtained an almost colorless gum, whose analysis indicated about 75 per cent addition. Rubber reacted just as with monochlorothiolacetic acid, derivatives of varying dichlorothiolacetate content being prepared by

leaving benzene solutions of the reactants plus a little ascaridole in the dark at room temperature for periods varying up to fifteen days. The products, undoubtedly containing the units (XVI, R = $CHCl_2$), were slightly harder and less elastic than similarly saturated monochlorothioacetates.

Reactions with trichlorothiolacetic acid.—This acid was added to cyclohexene, 1-methylcyclohexene, dihydromyrcene, and rubber, *trichlorothiolacetates* being formed readily in each case. *Methylcyclohexyl trichlorothiolacetate* was identi-

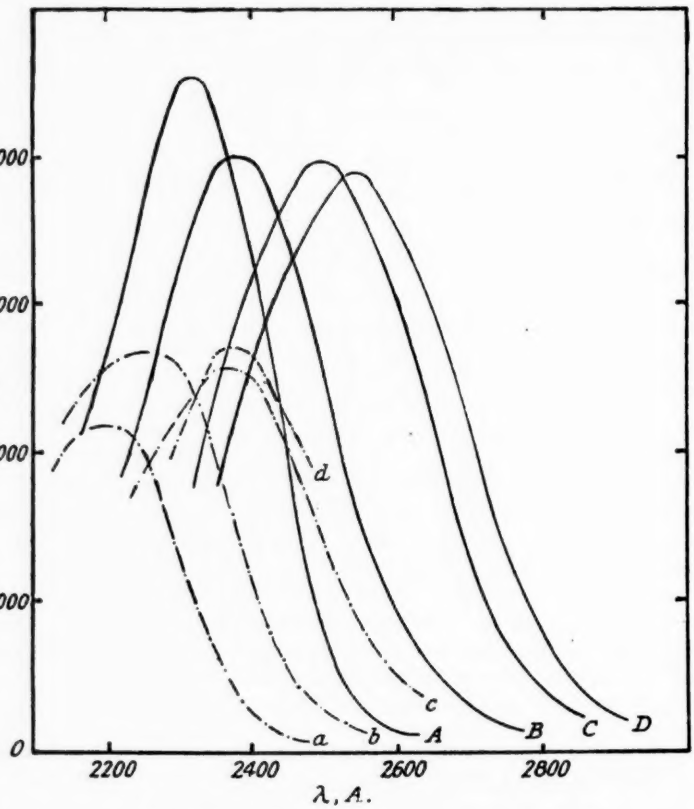


FIG. 1.—Except where otherwise stated, pure cyclohexane was used as the solvent.

a, Thiolacetic acid.
b, Monochlorothiolacetic acid.
c, Dichlorothiolacetic acid.
d, Trichlorothiolacetic acid.
A, 2-Methylcyclohexyl thiolacetate.
B, cyclohexyl chlorothiolacetate.
C, cyclohexyl dichlorothiolacetate.
D, cyclohexyl trichlorothiolacetate.

fied as (VI, R = CCl_3) by careful hydrolysis to a thiol which reacted with iodobenzene to give a phenyl sulfide, this yielding in turn on oxidation the sulfone (XI). Rubber reacted readily in the dark under peroxidic conditions, and more rapidly on irradiation with ultraviolet light. Following the trend described from the monochloro- to the dichlorothiolacetates, the products were still harder for similar extents of additions, the almost saturated compounds being tough thermoplastic materials resembling gutta-percha.

Absorption spectra.—In agreement with the spectra of some simple acetyl

sulfides already reported in the literature[6], the ultraviolet absorption curves of the four thioacids and their cyclohexyl esters shown in Figure 1 are characterized by intense absorption near 2300 A. (ϵ = 3800), which is evidently associated with conjugation between the carbonyl double bond and the unshared valency electrons of the sulfur atom, as will be more fully discussed elsewhere by H. P. Koch. As the acetyl hydrogen atoms are replaced by chlorine, both acids and esters display successive red shifts that are sufficiently marked to be characteristic of the degree of substitution. The acids absorb relatively less (as regards both wavelength and intensity) than the analogous esters, but the identical spectral type of the two series is in agreement with the infrared

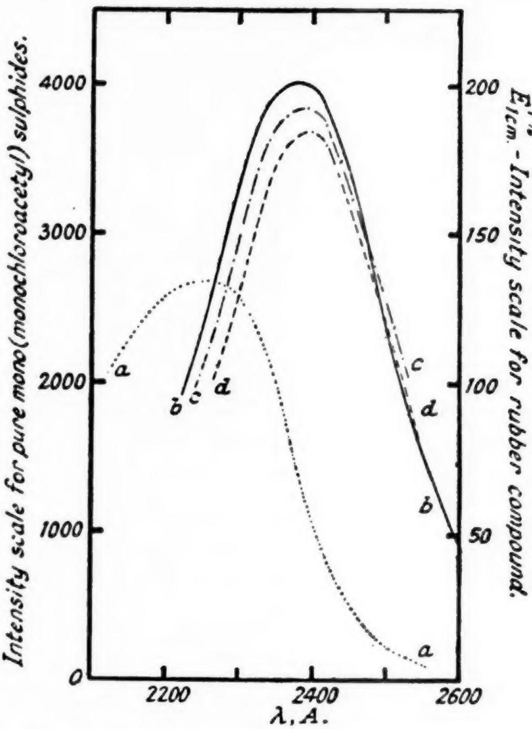


FIG. 2.—a, Monochlorothiolacetic acid. b, Cyclohexyl chlorothiolacetate. c, Dihydromyrcene chlorothiolacetate (in dioxan). d, Rubber chlorothiolacetate (in dioxan).

absorption evidence[7] that thiolacetic acid has the acetyl hydrogen sulfide structure, $CH_3 \cdot CO \cdot SH$. Comparison of the spectra of the esters prepared from cyclohexene and dihydromyrcene, illustrated in Figure 2 for the monochlorothiolacetate, and data for the other esters presented in the experimental section, show that both position and intensity of the bands are practically independent of the nature of the hydrocarbon radical attached to the sulfur atom. It is therefore possible to identify and to estimate the composition of the esters obtained from spectroscopically pure rubber by noting the position of the band head and comparing the maximum intensity with the standard intensity of the appropriate $\cdot CH_2 \cdot CHMe \cdot CH(S \cdot CO \cdot CX_3) \cdot CH_2 \cdot$ unit (X = H or Cl)

as derived from the dihydromyrcene adducts (see Figure 2). Such estimations are found to be in reasonable agreement with the results of elementary microanalysis, thus providing a further example of the value of this spectrographic method for both qualitative and quantitative analysis of complex products resulting from the addition of chromophoric groups to rubber and related olefins[8].

Discussion.—The additive reactivity of thiol acids exactly parallels that displayed by the thiols already considered[5], which have in common the scission of the thio compound at the S—H bond, the addition of the fragments contrary to Markownikoff's orientation rule, and the marked response to peroxide catalysis. However, thiol acids are definitely the more powerful reactants, as shown by the vigor of their reactions with the simpler olefins and by their ability to combine with rubber, which seems beyond the power of thiols. This fact agrees with the rough correlation pointed out earlier[5] between the activity of the addenda and the dissociation facility of the S—H links as measured by the acidity of the thio compound. The correlation, which is completely at variance with Ipatieff and Friedmann's deduction[2], noticeably extends to the thiol acids series itself in that thiolacetic acid requires added activation by ultraviolet light to combine with rubber whereas, with the stronger chlorothiolacetic acids, combination proceeds readily without this stimulus.

The decrease in reactivity in the olefin series from the cyclohexenes to rubber noted in the thiol reactions is again evident in the reactions with thiol acids, although the absolute reaction rates are widely different in the two cases. Attempts to trace the basis of this varying olefinic reactivity form the subject of further investigations in these laboratories.

Thiol acid addition clearly provides a very general method of introducing a substituent R contained in the group ·S·CO·CR into an olefin, and in some cases an easy preparation of thiols and derived thio compounds, such as sulfones. The mild reaction conditions, the absence of side reactions, and the ready control of the extent of addition, are particularly valuable when introducing substituents into long-chain olefins such as rubber with the object of modifying some properties, *e.g.*, resistance to solvents, and at the same time maintaining the high-molecular character responsible for the elastic properties. The extreme susceptibility of rubber to molecular degradation on a scale minute chemically, yet so often substantial physically, which is such a real barrier to useful modification, appears to have been effectively circumvented in the examples now presented.

THIOLACETIC ACID DERIVATIVES

Preparation of thiolacetic acid.—Clarke and Hartmann's method[9] was improved by using sulfuric acid as a catalyst instead of acetyl chloride or bromide, and by separating the thiol acid by distillation through an efficient Fenske column. Light absorption in cyclohexane: $\lambda_{max.}$ 2190 A. (ϵ = 2200).

Reaction of cyclohexene with thiolacetic acid.—A vigorous exothermic reaction occurred on shaking the acid (15.2 g.) with cyclohexene (16.4 g.). After 15 minutes, traces of unchanged reactants were removed by distillation at 50° under reduced pressure (water pump). The residue (29.2 g.) was *cyclohexyl thiolacetate* (I), b.p. 90°/14 mm. (Found: C, 60.1; H, 8.8; S, 20.2. $C_8H_{14}OS$ requires C, 60.6; H, 8.9; S, 20.3%).

Cyclohexanethiol (II).—The above ester (20 g.), ethyl alcohol (100 cc.), and 20% aqueous potassium hydroxide (100 cc.) were refluxed together for 15

minutes. The cooled solution was acidified (acetic acid), and the precipitated thiol collected *via* its ethereal solution and distilled. It (11.4 g.) had b.p. 157°/763 mm. (Found: C, 62.0; H, 10.55; S, 27.9. Calc. for $C_6H_{12}S$: C, 62.1; H, 10.3; S, 27.6%).

Cyclohexylphenyl sulfide (III).—The above thiol (4.6 g.) was dissolved in ethyl alcohol (30 cc.), and sodium (0.9 g.) added in small pieces. When all the metal had dissolved the alcohol was removed under reduced pressure, leaving solid cyclohexyl sodium sulfide. To this solid, iodobenzene (8.1 g.) and powdered copper (0.05 g.) were added, and the mixture was heated in an oil bath at 220° for 2 hours. Ether extraction of the cooled mixture gave cyclohexylphenyl sufide, b.p. 97–98°/0.05 mm. (Found: C, 75.0; H, 8.4; S, 16.6. Calc. for $C_{12}H_{16}S$: C, 75.0; H, 8.3; S, 16.65%); its identity was confirmed by oxidation by the standard procedure (see Part I) to cyclohexyl phenyl sulfone, m.p. 74°.

Cyclohexylthioglycolic acid (IV).—The thiol (II) (4.0 g.) was dissolved in a mixture of ethyl alcohol (22.8 cc.), potassium hydroxide (1.8 g.), and water (1.2 cc.), and the solution refluxed under nitrogen. An exactly equivalent solution of bromoacetic acid (4.4 g.) in 50% aqueous ethyl alcohol (1.9 cc.) was gradually added, and boiling continued for 4 hours. The mixture was then concentrated to dryness, the solid boiled in water (100 cc.) for 15 minutes, excess of hydrochloric acid added, and the boiling continued for a further 10 minutes. The precipitated oil, isolated by chloroform extraction, was the acid (IV) (4.8 g.), b.p. 136°/0.2 mm. (Found: C, 55.0; H, 8.25; S, 18.15; equiv., 180. Calc. for $C_8H_{14}O_2S$: C, 55.2; H, 8.05; S, 18.4%; equiv., 174), again identified by oxidation to its sulfone, m.p. 82° (*cf.* Part I).

Reaction of 1-*methylcyclohexene with thiolacetic acid.*—The olefin (9.6 g.) reacted vigorously with the acid (7.6 g.) to give 2-*methylcyclohexyl thiolacetate* (VI, R = Me), b.p. 110°/14 mm. (16.2 g.) (Found: C, 62.45; H, 9.3; S, 19.0. $C_9H_{16}OS$ requires C, 62.75; H, 9.3; S, 18.6%). Light absorption in cyclohexane: $\lambda_{max.}$ 2315 A. (ϵ = 4500).

2-*Methylcyclohexanethiol* (VIII).—Hydrolysis of the above ester (7 cc.) as described for the corresponding cyclohexyl homolog gave the *thiol* (4.25 g.), b.p. 165° (Found: C, 64.2; H, 10.7; S, 24.8. $C_7H_{14}S$ requires C, 64.6; H, 10.8; S, 24.6%).

2-*Methylcyclohexylphenyl sulfide.*—Prepared from the above thiol and iodobenzene as described for the cyclohexyl derivative, this sulfide had b.p. 108°/0.05 mm. (Found: S, 15.2. Calc. for $C_{13}H_{18}S$: S, 15.55%), and readily yielded the corresponding sulfone, m.p. 108°, on oxidation.

2-*Methylcyclohexylthioglycolic acid.*—This sulfide was prepared by treating the thiol (VIII) with bromoacetic acid in the manner previously described, b.p. 130°/0.05 mm. (Found: C, 57.6; H, 8.8; S, 16.7. Calc. for $C_9H_{16}O_2S$: C, 57.4; H, 8.4; S, 17.0%). Oxidation gave the acid sulfone, m.p. 96°.

Reaction of dihydromyrcene with thiolacetic acid.—(a) The olefin (8 g.) was shaken for 30 minutes with the quantity of thio acid (4.4 g.) required to saturate one double bond. Fractional distillation of the oil so obtained gave: (1) unchanged reactants containing a little sulfide, b.p. < 100°/12 mm. (1.6 g.); (2) *dihydromyrcene monothiolacetate* (XIII, R = Me), b.p. 128°/10 mm. (4.7 g.) (Found: C, 67.35; H, 10.35; S, 14.6. $C_{12}H_{22}OS$ requires C, 67.3; H, 10.3; S, 14.95%) [light absorption in cyclohexane: $\lambda_{max.}$ 2315 A. (ϵ = 4750); in dioxan, $\lambda_{max.}$ 2330 A. (ϵ = 4600)]; (3) a mixture of the mono- and diadducts, b.p. 100–122°/0.1 mm. (2.7 g.).

(b) The reaction was repeated but with excess of thiolacetic acid (17 g. with 14 g. of hydrocarbon). The product on fractionation gave: (1) unchanged reagents, b.p. < 80°/0.1 mm. (1.6 g.); (2) *dihydromyrcene bisthiolacetate* (XIV; R = Me) containing a trace of the monoacetate, b.p. 110–113°/0.1 mm. (4.2 g.) (Found: C, 58.2; H, 9.05. $C_{14}H_{26}O_2S_2$ requires C, 57.85; H, 8.95%); (3) *dihydromyrcene bisthiolacetate,* b.p. 125°/0.05 mm. (17.8 g.) (Found: C, 57.9; H, 9.0; S, 21.75. $C_{14}H_{26}O_2S_2$ requires C, 57.85; H, 8.95; S, 22.05%) [light absorption in cyclohexane: $\lambda_{max.}$ 2315 A. (ϵ = 4750); in dioxan, $\lambda_{max.}$ 2330 A. (ϵ = 4400)]; (4) residue (4.1 g.).

Dihydromyrcenethiol (XV).—The ester (XIV, R = Me) on alkaline hydrolysis in the usual way gave the parent *dithiol,* a colorless oil, b.p. 128°/25 mm. (Found: C, 58.7; H, 10.6; S, 30.3; $C_{10}H_{22}S_2$ requires C, 58.2; H, 10.7; S, 31.1%).

Reaction of squalene with thiolacetic acid.—The hydrocarbon (2 g.) shaken with the acid (2 g.) for 30 minutes produced a reaction rather less exothermic than that with cyclohexene. Unreacted thiolacetic acid was removed at 100°/10^{-5} mm., leaving a colorless viscous syrup (Found: S, 12.05. Calc. for 36% addition: S, 12.05%).

Reaction of rubber with thiolacetic acid.—(1) Three Pyrex tubes (diam. 1.5 cm.), each containing sol rubber (1 g.), benzene (25 cc.), and thiolacetic acid (1 cc.), were sealed in a vacuum, placed 6 inches from a mercury-vapor lamp, and irradiated for 4, 8, and 16 hours, severally. The products isolated by precipitation with ethyl alcohol were similar white rubbers (Found, respectively: C, 71.8; H, 10.1; S, 11.85; C, 69.8; H, 9.8; S, 14.2; C, 67.7; H, 9.55; S, 15.1. 50% addition requires C, 68.0; H, 9.45; S, 15.1%).

(2) A reaction mixture containing more thio acid (2.5 cc.) was irradiated for 6 hours with ultraviolet light, and the product isolated as before (Found: S, 15.5. Calc. for 52% addition: S, 15.5%). Light absorption in dioxan: $\lambda_{max.}$ 2330 A., $E^{1\%}_{1\,cm.}$ = 205; $[C_5H_8,\ CH_3\cdot CO\cdot SH]_n$ requires $E^{1\%}_{1\,cm.}$ = 10 ϵ/unit M = 10 × 4500/144 = 310; hence amount of addition is 48%.

(3) An exactly similar reaction mixture to that used in (2) was irradiated with the mercury-vapor lamp for 16 hours. The product was a hard white solid (Found: C, 58.95; H, 9.0; S, 20.7. Calc. for 86% addition: C, 60.3; H, 8.6; S, 20.7%).

(4) The reaction mixture as used in (1) was illuminated for 16 hours with a 300-watt tungsten-filament lamp. A white rubber resulted superficially indistinguishable from the starting material (Found: S, 0.6%, corresponding to 1.3% addition).

(5) The reaction mixture as in (1) but containing ascaridole (0.025 g.) was sealed under vacuum and heated in a Carius furnace at 130° for 3 hours. The rubber product again showed little change (Found: S, 1.5%).

(6) A reaction mixture as in (5) was sealed under vacuum, and left in the light of the laboratory for 1½ years. The product showed 26% addition (Found: S, 9.5. Calc.: S, 9.5%).

(7) The reaction mixture as used in (1) was illuminated with a carbon arc for 45 hours (Found: C, 69.96; H, 9.9; S, 12.8%, corresponding to 39% addition).

(8) Some experiments were conducted on a larger scale, using an annular form of apparatus (external diam. 6 cm., internal diam. 3.5 cm., length 25 cm.) in which the ultraviolet lamp was suspended, the reaction mixture being sealed under vacuum in the outer jacket and cooled with a rapid stream of water.

Milled rubber (*M*, 150,000) enabled more concentrated solutions to be used. Rubber (15 g.), dissolved in benzene (150 cc.) containing thiolacetic acid (15 cc.), irradiated in a vacuum under these conditions for 9 hours, yielded a white rubber (23 g.) (Found: S, 15.7. Calc. for 53% addition: S, 15.7%). A repeat experiment using 25 cc. of the acid gave 76% addition (Found: C, 61.8; H, 8.8; S, 19.3. Calc.: C, 62.0; H, 8.8; S, 19.3%).

Rubber thiol (XVII).—Finely cut *thiolacetyl rubber* (1 g.) (Found: C, 67.7; H, 9.55; S, 15.1. $C_{12}H_{20}OS$ requires C, 68.0; H, 9.45; S, 15.1% was dissolved in benzene (35 cc.) and ethyl alcohol (10 cc.) containing sodium (0.01 g.). The mixture was shaken for 6 hours at room temperature and then poured into excess ethyl alcohol. The *thiol* was precipitated as a fibrous white solid, which was thoroughly washed with water (Found: S, 18.7. $C_{10}H_{18}S$ requires S, 18.8%).

MONOCHLOROTHIOLACETIC ACID DERIVATIVES

Reaction of cyclohexene with chlorothiolacetic acid.—The acid (22 g.), b.p. 48°/16 mm.[9] Light absorption in cyclohexane: $\lambda_{max.}$ 2255 A. (ϵ = 2650) when added to cyclohexene (17 g.) produced an immediate and vigorous exothermic reaction. The product, when freed from starting materials by heating at 90°/14 mm., was *cyclohexyl chlorothiolacetate*, b.p. 132°/14 mm. (Found: C, 49.95; H, 6.85; S, 16.4; Cl, 18.4. $C_8H_{13}OClS$ requires C, 49.8; H, 6.75; S, 16.6; Cl, 18.4%). Light absorption in cyclohexane: $\lambda_{max.}$ 2380 A. (ϵ = 4000).

Hydrolysis of cyclohexyl chlorothiolacetate.—The ester (6.75 g.), ethyl alcohol (35 cc.), and 20% aqueous potassium hydroxide were refluxed for 4 hours, and after the procedure described for the corresponding thiolacetate, cyclohexylthioglycolic acid (5.3 g.) readily separated, b.p. 120°/0.1 mm. (Found: C, 55.25; H, 8.3; S, 18.25; equiv., 178. Calc, for $C_8H_{14}O_2S$: C, 55.2; H, 8.05; S, 18.4%; equiv., 174). This specimen gave the authentic sulfone, m.p. 82°, on oxidation.

Reaction of 1-*methylcyclohexene with chlorothiolacetic acid.*—Reaction between the hydrocarbon (9.6 g.) and the acid (11 g.) proceeded vigorously to give 2-methylcyclohexyl chlorothiolacetate (VI, R = CH_2Cl), b.p. 137°/11 mm. (18.7 g.) (Found: S, 14.85; Cl, 18.5. $C_9H_{15}OClS$ requires S, 15.5; Cl, 17.2%).

Hydrolysis of 2-*methylcyclohexyl chlorothiolacetate.*—The ester, hydrolyzed as described for the cyclohexene derivative, gave 2-methylcyclohexylthioglycolic acid, b.p. 129°/0.05 mm. (Found: C, 57.45; H, 8.65; S, 16.95; equiv., 184. Calc. for $C_9H_{16}O_2S$: C, 57.4; H, 8.4; S, 17.0%; equiv., 186), identified by its crystalline sulfone, m.p. 96°.

Reaction of dihydromyrcene with chlorothiolacetic acid.—The hydrocarbon (10 g.) was shaken with the acid (5.5 g.) for 15 minutes. Distillation of the product gave the following fractions: (1) unchanged reactants, b.p. <100°/14 mm. (3.7 g.); (2) *dihydromyrcene chlorothiolacetate* (XIII, R = CH_2Cl), b.p. 99°/0.1 mm. (9.2 g.) (Found: C, 57.35; H, 8.4; S, 12.7; Cl, 13.65. $C_{12}H_{21}OClS$ requires C, 58.1; H, 8.6; S, 12.4; Cl, 14.2%) [light absorption in dioxan: $\lambda_{max.}$ 2385 A. (ϵ = 3850)]; (3) mainly dihydromyrcene bischlorothiolacetate contaminated with some of the monoadduct, b.p. 108–174°/0.1 mm. (Found: C, 49.8; H, 7.0; Cl, 19.0. Calc. for mixture of 77% diadduct and 23% monoadduct: C, 49.4; H, 7.1; Cl, 18.5%).

Reaction of squalene with chlorothiolacetic acid.—Squalene (10 g.) was shaken with the acid (17 g.) for 30 minutes, the exothermic reaction then having ceased.

Unreacted acid was removed in a vacuum (10^{-5} mm.) at 100°, leaving a pale green, viscous syrup evidently consisting of a mixture of squalene chlorothiolacetates (Found: S, 15.8; Cl, 17.2. Calc. for 74% addition: S, 15.8; Cl, 17.3%).

Reaction of rubber with chlorothiolacetic acid.—The following are a representative selection of the many experiments carried out with rubber and this acid. (1) A solution of sol rubber (1 g.), benzene (25 cc.), monochlorothiolacetic acid (1.5 cc.), and ascaridole (0.05 g.) was sealed under vacuum and illuminated for 6 hours with the mercury-vapor lamp. The product precipitated by ethyl alcohol was a hard white solid (2.2 g.) (Found: C, 48.7; H, 6.6; S, 17.1; Cl, 19.0. Calc. for 88% addition: C, 49.1; H, 6.4; S, 17.1; Cl, 19.0%). (2) A reaction mixture similar to that used in (1) was evacuated and left in the dark at room temperature for 7 days. The product showed only 58.5% addition (Found: S, 13.75; Cl, 15.6. Calc.: S, 14.1; Cl, 15.65%). Light absorption in dioxan, $\lambda_{max.}$ 2390 A., $E^{1\%}_{1\,cm.} = 180$. $[C_5H_8Cl \cdot CH_2 \cdot CO \cdot SH]_n$ requires $E^{1\%}_{1\,cm.} = 10\epsilon/\text{unit } M = 10 \times 3850/178.5 = 216$, and hence amount of addition is 65.5%. Imbibition of aviation fuel[10], 40%. (3) Five tubes each containing milled rubber (M, 150,000) (1 g.), benzene (10 cc.), monochlorothiolacetic acid (1 cc.), and ascaridole (0.05 g.) sealed in a vacuum were kept at room temperature for 4, 6, 10, 18 and 34 days, severally. The products were precipitated and dried, and then had the properties and analytical values given in the table. (4) The catalytic activity of different peroxides was investigated as follows. To one of four tubes containing the basic reaction mixture as in (3) was added ascaridole, to another benzoyl peroxide, to the third *tert*-butyl hydroperoxide, and no addition was made to the fourth. These tubes were sealed under vacuum and kept at room temperature in the dark for 4 days.

The amounts of aviation fuel imbibed by the respective products, isolated in each case by alcohol precipitation, are shown in the table, and since the imbibition varies inversely as the extent of thio acid addition the catalytic activities of the various peroxides in promoting this addition are clearly seen. Other series of experiments carried out with different peroxide concentrations all showed the same order.

Reaction time (days)	Catalyst	S (%)	Cl (%)	Liquid imbibed, %: Light petroleum (b.p. 40–60°)	Liquid imbibed, %: Aviation fuel
4	Ascaridole	12.5	14.3	5	53
6	Ascaridole	13.1	15.1	2	43
10	Ascaridole	15.5	17.4	1	36
18	Ascaridole	15.9	18.0	—	27
34	Ascaridole	16.0	17.9	—	24
4	Ascaridole	12.5	14.3	5	53
4	(None)	—	—	—	(Product dissolved)
4	Benzoyl peroxide	—	—	—	190
4	*tert*-Butyl hydroperoxide	—	—	—	72

(5) Larger-scale experiments were carried out in the following way. Milled rubber (50 g.) was dissolved in benzene (500 cc.) containing monochlorothiolacetic acid (36 cc.) and ascaridole (2.5 cc.), and the solution kept in the absence of air at room temperature and in the dark for 15 days. After removal of the benzene by steam-distillation, the product which separated was washed with ethyl alcohol and dried (Found: C, 56.45; H, 7.3; S, 13.2; Cl, 15.3. Calc. for 56% addition: C, 56.0; H, 7.4; S, 13.8; Cl, 15.3%). Imbibition of aviation fuel, 50%.

DICHLOROTHIOLACETIC ACID DERIVATIVES

Preparation of dichlorothiolacetic acid.—Arndt and Berkir's method[9] for the preparation of monochlorothiolacetic acid was adapted to the present synthesis. A rapid stream of dry hydrogen sulfide was passed through a cooled (0°), well stirred solution of dichloroacetyl chloride (500 g.) and powdered dry aluminum chloride (10 g.) until the evolution of hydrogen chloride had ceased (6–7 hours). Distillation of the reaction mixture yielded *dichlorothiolacetic acid* as a pale green liquid, b.p. 56°/16 mm. (315 g.) (Found: C, 16.55; H, 1.8; S, 21.65; Cl, 49.4. $C_2H_2OCl_2S$ requires C, 16.55; H, 1.4; S, 22.05; Cl, 48.9%). Light absorption in cyclohexane: $\lambda_{max.}$ 2365 A. (ϵ = 2550).

Reaction of cyclohexene with dichlorothiolacetic acid.—The usual reaction between the hydrocarbon (25 g.) and the thio acid (42 g.) proceeded on shaking. *Cyclohexyl dichlorothiolacetate* was obtained as the sole product, b.p. 148°/12 mm. (63 g.) (Found: C, 42.4; H, 5.5; Cl, 31.9. $C_8H_{12}OCl_2S$ requires C, 42.3; H, 5.3; Cl, 31.3%). Light absorption in cyclohexane: $\lambda_{max.}$ 2495 A. (ϵ = 3950). Hydrolysis with alcoholic alkali afforded an unidentified viscous oil, v.p. >220°/758 mm. No cyclohexanethiol could be isolated.

Reaction of dihydromyrcene with dichlorothiolacetic acid.—The hydrocarbon (8 g.) was shaken for 15 minutes with the thio acid (12 g.). Fractional distillation of the oily product gave: (1) unchanged reactants containing a little acetate, b.p. <100°/0.1 mm. (2.5 g.); (2) *dihydromyrcene dichlorothiolacetate* (XIII, R = $CHCl_2$) (4.6 g.), b.p. 118°/0.1 mm. (Found: S, 11.3; Cl, 25.1. $C_{12}H_{20}OCl_2S$ requires S, 11.3; Cl, 25.1%) [light absorption in dioxan: $\lambda_{max.}$ 2505 A. (ϵ = 3900)]; (3) a mixture of mono- and diadducts (0.8 g.), b.p. 160–180°/0.1 mm. (Found: C, 43.7; H, 5.8; S, 14.2. Calc. for a mixture 38% $C_{12}H_{20}OCl_2S$ and 62% $C_{14}H_{22}O_2Cl_4S_2$: C, 43.7; H, 5.9; S, 13.6%); (4) residue (12 g.).

Reaction of squalene with dichlorothiolacetic acid.—After the hydrocarbon (2 g.) had been shaken with the thio acid (4.5 g.) for 30 minutes, unreacted acid was removed at 100°/10^{-5} mm., leaving a pale green gum (Found: C, 43.2; H, 5.6; Cl, 29.55. Calc. for 75% addition: C, 43.8; H, 5.6; Cl, 30.0%).

Reaction of rubber with dichlorothiolacetic acid.—(1) A solution of sol rubber (1 g.), benzene (30 cc.), ascaridole (0.05 g.), and acid (1.5 cc.) was sealed under vacuum and left in the dark at room temperature for 10 days. The viscosity of the solution increased almost to the point of gelation. The product obtained by precipitation with ethyl alcohol, followed by extraction (Soxhlet) with methyl alcohol in an atmosphere of nitrogen for 24 hours, was a white rubber (2.5 g.) (Found: C, 44.4; H, 5.5; S, 13.15; Cl, 29.5. Calc. for 71% addition: C, 44.8; H, 5.5; S, 13.3; Cl, 29.5%). This material showed extensive but sluggish elastic behavior. (2) Sol rubber (0.5 g.), benzene (20 cc.), ascaridole (0.02 g.), and the thio acid (1.0 cc.) were kept under vacuum for 5 days at room temperature in the dark. The product isolated in the usual way was a white rubber (Found: S, 10.5; Cl, 23.75. Calc. for 44.4% addition: S, 10.7; Cl, 23.75%).

TRICHLOROTHIOLACETIC ACID DERIVATIVES

Preparation of trichlorothiolacetic acid.—The acid chloride (500 g.), treated in the usual manner, afforded a mixture which on fractional distillation gave: (1) trichloroacetyl chloride containing some of the thio acid, b.p. 44–50°/11 mm. (85 g.); (2) *trichlorothiolacetic acid*, b.p. 57°/11 mm. (348 g.), an almost

colorless liquid (Found: C, 13.4; H, 0.6; S, 17.55; Cl, 59.7. C_2HOCl_3S requires C, 13.4; H, 0.6; S, 17.8; Cl, 59.3%) [light absorption in cyclohexane: $\lambda_{max.}$ 2375 A. (ϵ = 2700)]; (3) residue (43 g.).

Reaction of cyclohexene with trichlorothiolacetic acid.—The solution of the olefin (8.2 g.) in the acid (18 g.) was shaken for 15 minutes. The resulting oil on distillation gave exclusively *cyclohexyl trichlorothiolacetate*, b.p. 151°/12 mm. (25.1 g.) (Found: C, 36.95; H, 4.3; S, 12.25; Cl, 40.6. $C_8H_{11}OCl_3S$ requires C, 36.7; H, 4.2; S, 12.25; Cl, 40.75%). Light absorption in cyclohexane: $\lambda_{max.}$ 2540 A. (ϵ = 3900).

Reaction of 1-methylcyclohexene with trichlorothiolacetic acid.—*2-Methylcyclohexyl trichlorothiolacetate* (VI, R = CCl_3), b.p. 96°/0.1 mm. (Found: C, 39.65; H, 5.15; S, 11.3; Cl, 38.4. $C_9H_{13}OCl_3S$ requires C, 39.2; H, 4.7; S, 11.65; Cl, 38.6%), was prepared in almost theoretical yield from the hydrocarbon and the thio acid just as described for the cyclohexene derivative. Submitted to the hydrolytic procedure described for cyclohexyl thiolacetates, the ester gave an oil which reacted with iodobenzene to give *2-methylcyclohexylphenyl sulfide*, b.p. 105°/0.015 mm. (Found: C, 76.0; H, 8.9; S, 15.3. Calc. for $C_{13}H_{18}S$: C, 75.6; H, 8.75; S, 15.55%), identified by its crystalline *sulfone*, m.p. 108°.

Reaction of dihydromyrcene with trichlorothiolacetic acid.—Reaction of the hydrocrabon (11 g.) and the thio acid (10 g.) in the usual way, followed by distillation, gave: (1) unreacted dihydromyrcene (0.6 g.), b.p. <100°/15 mm., (2) *dihydromyrcene trichlorothiolacetate* (XIII, R = CCl_3) (12.1 g.), b.p. 119°/0.05 mm. (Found: C, 45.45; H, 6.15; S, 9.7; Cl, 33.3. $C_{12}H_{19}OCl_3S$ requires C, 45.4; H, 6.0; S, 10.1; Cl, 33.6%) [light absorption in dioxan: $\lambda_{max.}$ 2550 A. (ϵ = 3900)]; (3) a mixture of mono- and diadducts (0.6 g.), b.p. 120–155°/0.05 mm. (Found: S, 10.25; Cl, 34.5. Calc. for mixture of 90% $C_{12}H_{19}OCl_3S$ and 10% $C_{14}H_{20}O_2Cl_6S_2$: S, 10.45; Cl, 34.5%); (4) residue (6.4 g.).

Reaction of rubber with trichlorothiolacetic acid.—(1) Sol rubber (1 g.), dissolved in benzene (30 cc.) containing the thio acid (1 cc.; *i.e.*, insufficient to saturate all the double bonds) and ascaridole (0.05 g.), was sealed under vacuum and kept at room temperature for 15 days. The product, isolated by alcohol precipitation, was a white rubberlike material (2.1 g.) (Found: C, 48.1; H, 5.5; S, 9.4; Cl, 31.7. Calc. for 42.5% addition: C, 48.7; H, 5.8; S, 9.4; Cl, 31.2%). (2) A similar solution but containing twice the amount of thio acid was kept for 7 days under similar conditions. The product was a hard white solid (Found: S, 11.95; Cl, 39.8. Calc. for 75.6% addition: S,11.95; Cl, 39.8%). Light absorption in dioxan: $\lambda_{max.}$ 2555 A., $E^{1\%}_{1\,cm.}$ = 140; $[C_5H_8, CCl_3\cdot CO\cdot SH]_n$ requires $E^{1\%}_{1\,cm.} = 10\ \epsilon/\text{unit}\ M = 10 \times 3900/248 = 155$, and hence amount of addition is 72%. (3) An exactly similar solution to (2) was sealed under vacuum in a Pyrex tube (diam. 1.5 cm.), placed 6 inches from the mercury-vapor lamp, and irradiated for 6 hours. The product was a hard, brittle solid (Found: C, 36.0; H, 4.1; S, 12.8; Cl, 40.2. Calc. for 87.6% addition: C, 36.0; H, 4.0; S, 12.4; Cl, 41.4%).

SUMMARY

Cyclohexene, 1-methylcyclohexene, dihydromyrcene, squalene, and rubber[11] combine additively with the above named thio acids, the reactions proceeding similarly to, but more easily than, those reported earlier for thiols. The parallelism noted previously between the ease of thiol addition and the facility of proton removal from the S—H bond, as measured by acidity, not only extends to thiol acids generally, but also accords with the fact that among the latter

themselves the more acid chloro-substituted compounds are the more active addenda. A reactivity order, cyclohexenes > dihydromyrcene > squalene > rubber, is again evident, but whereas this serves to make the last olefin inert towards thiols, yet thio acid adducts are readily prepared, and these are of considerable technological interest as oil- and gasoline-resistant rubbers.

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REFERENCES

1 Holmberg, *Arkiv. Kemi. Min. Geol.* **12B**, No. 47 (1938).
2 Ipatieff and Friedmann, *J. Am. Chem. Soc.* **61**, 71 (1939).
3 Sjöberg, *Ber.* **74**, 64 (1941).
4 Holmberg and Schjönberg, Arkiv. Kemi. Min. Geol. 14 A, No. 7 (1940).
5 Cunneen, *J. Chem. Soc.* **1947**, p. 36 (Part I).
6 Sjöberg, *Z. physik. Chem.* **52B**, 909 (1942).
7 Sheppard and Sutherland, private communication.
8 Cunneen, Farmer and Koch, *J. Chem. Soc.* **1943**, p. 472.
9 Arndt and Berkir, *Ber.* **63**, 2390 (1930).
10 Aviation fuel RDEF/75, containing approximately 35 per cent of aromatic hydrocarbons, was used for the imbibition tests.
11 British and U. S. patent specifications pending.

CRACK GROWTH IN GR-S TREAD STOCKS

RELATION TO STATE OF CURE AND COMPOSITION *

A. E. Juve

The B. F. Goodrich Company, Akron, Ohio

One of the most serious deficiencies of GR-S vulcanizates is their poor resistance to crack growth during flexing. This weakness is a major concern in the use of GR-S in tire treads, but it is also a serious handicap in other products which are subjected in service to repeated flexing. A second serious deficiency is their high heat generation during flexing.

It has been the general experience of tire technologists that GR-S treads, which possess the properties usually associated with an undercure or a low state of cure, give good resistance to crack growth[1]. These properties are low modulus, high elongation, high permanent set, low resilience, and high temperature build-up on flexing. As these properties are changed by advancing the state of cure, the resistance to crack growth declines precipitously, while the temperature build-up improves. A satisfactory solution to the problem must provide a more favorable balance between these properties, either by an improved compounding technique or by the development of an improved polymer. It was the purpose of the work reported here to study the relation between these two properties using the conventional De Mattia crack-growth test and the Goodrich flexometer test[2] to measure the properties.

The choice of the latter test was dictated by two considerations. First, its use focuses attention on one of the properties in which GR-S is deficient, and, second, it is a good measure of the relative state of cure. Relations similar to the one developed here could, no doubt, be developed with any of the test methods ordinarily used to measure or estimate the state of cure, provided they are reasonably sensitive.

TEST METHODS

The temperature rise measurements used in this study were run in the Goodrich flexometer at 212° F, with a 55-pound load and a stroke of 17.5 per cent. ΔT is the rise in temperature above 212° F after 25 minutes in the machine. All crack-growth tests, except where otherwise noted, were run on a De Mattia flexing machine at 300 cycles per minute and a stroke of $2\frac{1}{4}$ inches, in a room maintained at 82° F and at 45 per cent relative humidity. The crack was initiated by means of a No. 2 needle and the number of cycles recorded for the crack to grow to an arbitrary rating of 8. Unless otherwise indicated, this is the flexing life. A high value indicates a low rate of crack growth and a low value a high rate. A rating of 0 is no growth, and 10 is complete failure.

QUALITY INDEX AS CRACK GROWTH-HYSTERESIS RELATION

A wide variety of GR-S tread compounds on which crack-growth and temperature-rise data had been obtained were first studied by plotting the values for

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temperature rise against the logarithm of the flexing life. The curve representing the median value for this series of observations and the two parallel curves representing the spread, which included 90 per cent of the values, are illustrated in Figure 1. The equation for the average curve is:

$$\log \text{flexing life} = 0.0126\Delta T + 4.28 \tag{1}$$

The compounds included in this group which numbered 268, represented variations in sulfur ratio, accelerator ratio, kind of accelerator, degree of cure, plasticized and crude GR-S, aging of the crude GR-S at various temperatures, aging of the vulcanizates, and minor variations in the GR-S. All compounds, however, contained 45 to 50 parts of either EPC or MPC black. As a check the data for an additional group of 146 compounds were plotted, and it was found that all values fell within the limits shown, and that 71 of the cases were above the average line and 74 cases below.

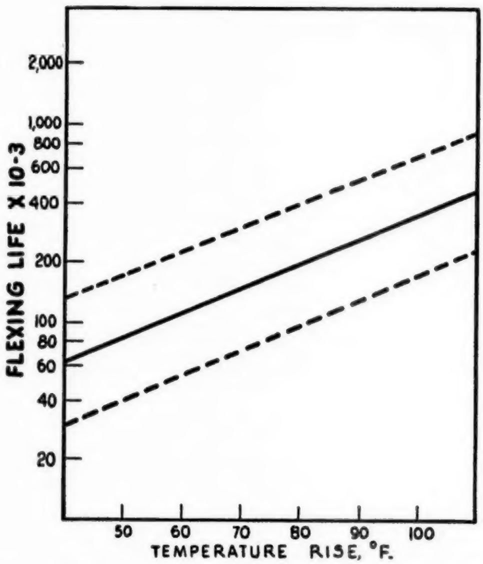

Fig. 1.—Flexing *vs.* temperature rise for state-of-cure variations.

Undoubtedly cases were included in this plot which should not have been included in the light of subsequent findings; thus the spread in results for a particular level of temperature rise is somewhat wider than it should be. Also it should not be implied that, if a careful examination were made, one would not find a consistent difference between a stock containing 45 parts of EPC black and one containing 50 parts of MPC black.

However, with these considerations discounted, there is still an appreciable dispersion of crack-growth results for a specific temperature rise level, which would indicate either poor precision of the test methods or less dependence between the two properties than is indicated by Equation 1. Subsequent tests have shown that the former is the case. The temperature-rise measurement is subject to a small error, but the precision of the crack-growth test is poor. Also the two measurements are made on different specimens cured in different

molds and, frequently, on different days. The cure rate of the stocks may vary appreciably from day to day as the result of a gain or loss in moisture resulting from humidity changes[3]. Also, the hysteresis specimen is either cut from a 1-inch thick block or molded into a 0.7-inch-diameter, 1-inch high pellet, and the state of cure in these thicker specimens may not be strictly in the same relation to that of the thinner flexing specimens when different compounds are being compared.

TABLE I

EFFECT OF CURING TIME

(Recipe, parts by weight: GR-S 100, Captax 1.0, DPG 0.2, sulfur 2, zinc oxide 5, Age-Rite-HP 1, MPC black 47, Paraflux 10)

Cure			Log flex	
Temperature (° F)	Time (min.)	ΔT(° F)	Observed	Calculated
260	60	106	5.9	5.6
	90	78.5	5.5	5.3
	120	63	5.1	5.2
	180	46.5	4.9	4.9
	240	43.5	4.7	4.8
	300	42	4.6	4.8
280	25	112	5.6	5.7
	40	81	5.0	5.3
	60	59	4.9	5.0
	90	45.5	4.6	4.8
	120	43	4.6	4.8
300	15	96	5.9	5.5
	25	65	4.9	5.1
	40	46	4.8	4.9
	60	43	4.6	4.8

Table I illustrates the application of Equation 1 to variations in time of cure for a typical GR-S tread stock cured for varying lengths of time at three curing temperatures.

TABLE II

EFFECT OF VARIATIONS IN SULFUR AND ACCELERATOR RATIOS

(Base recipe, parts by weight: GR-S 100, zinc oxide 5, MPC black 47, Paraflux 10, Age-Rite-HP 1)

Compound	Sulfur ratio	Accelerator ratio (Captax/ 0.2 DPG)	ΔT(° F)	Log flex Observed	Log flex Calculated
A	1	1.5	118	5.6	5.8
B	1	2.0	123	5.6	5.8
C	1	2.5	76	5.6	5.2
D	2	0.75	80	5.1	5.3
E	2	1.0	68	4.9	5.1
F	2	1.5	62	5.0	5.1
G	3	0.5	67	4.9	5.1
H	3	0.75	45	4.8	4.8
I	3	1.0	48	4.9	4.9

Table II gives data comparing the calculated and observed flex life for a series of GR-S tread stocks in which the sulfur and accelerator ratios were varied.

In the Goodrich flexometer test, variations of the type listed in the composition or cure, which affect the modulus (300 per cent static modulus), also

affect the rise in temperature. A reduction in modulus results in a higher rise in temperature, and an increase results in a lower rise in temperature. For all such variations in recipe, Equation 1 represents the temperature rise–crack growth relation. However, other variations in composition may be made for which this equation does not apply. These are changes which simultaneously either increase or decrease both temperature rise and modulus. Changes of this type include variations in the concentration of carbon black and the use of certain high melting resins or pitches.

On the basis of data of 774 compounds, representing variations in composition of this type, an empirical equation has been derived which represents the approximate relation between crack growth, hysteresis temperature rise, and the 300 per cent static modulus:

$$\log \text{flexing life} = 5.42 + \frac{\Delta T}{336} - \frac{M}{2000} \tag{2}$$

To illustrate the application of this equation, the EPC black loading in a GR-S tread type recipe was varied from 20 to 75 PHR (parts per hundred on the rubber). Table III shows the modulus, the temperature rise, the observed flexing and the flexing calculated with Equation 2.

TABLE III

EFFECT OF VARIATIONS IN LOADING OF EPC BLACK

(Recipe, parts by weight: GR-S 100, Paraflux 10, zinc oxide 5, Age-Rite-HP 1, sulfur 1.75, Santocure 1.2, EPC black as shown)

Loading (PHR)	300% modulus (lb./sq. in.)	ΔT(° F)	Log flex	
			Observed	Calculated
20	350	46	5.5	5.4
30	500	54	5.4	5.3
40	800	72	5.3	5.2
50	1000	94	5.2	5.2
60	1650	115	4.9	4.9
75	2450	*	—	—

* Blew out during the test.

Although Equation 1 is satisfactory for recipe variations which result in variations in the state of cure and for time of cure variations, Equations in the state of cure and for time of cure variations, Equation 2 is more accurate for applications to all other recipe variations which do not involve carbon blacks or pigments other than EPC or MPC. In some compounding studies and, in particular, in the evaluation of experimental polymers, it is frequently impossible to be certain that changes in temperature rise are due to state of cure variations or to inherent differences in the hysteresis properties of the mixture or the polymer.

A more favorable balance between these two properties may be evidenced by an improved flexing life at the same temperature rise level or an improved temperature rise at the same flexing life level, or various intermediate combinations. As a convenient expression of the degree of improvement obtained, either by compounding modifications or by polymer improvements, the author uses the term *quality index*, which is defined as the ratio of the observed flexing life for the experimental material to either: (1) the calculated flexing life, using Equation 1, of a GR-S tread compound containing the normal loading of EPC or MPC black and having a temperature rise equal to that of the experimental

material, or (2) the calculated flexing life, using Equation 2, of a GR-S tread compound containing EPC or MPC black and having a modulus and temperature rise equal to that of the experimental material.

A high quality index for a particular polymer, for example, does not necessarily mean that the overall performance of a tire tread made from it will be superior to that of a GR-S tread. The quality index indicates only the relative excellence with respect to crack growth and temperature rise, and gives no information on the numerous other properties on which the performance of a tire tread depends.

By this definition the quality index for a GR-S tread stock when compounded within the limits given should be 1.00—that is, the calculated and observed flexing values should be the same. However, for several reasons there may be differences which lead to quality indexes higher or lower than 1.00. For the reasons already given, in discussing the precision of test methods, one would expect an appreciable variation due to this cause. In addition, the composition and quality of commercial GR-S is not a constant. For example, the styrene ratio has not been permanently fixed, and this, as will be shown later, has a pronounced effect on this balance of properties. Also, the degree of carbon black dispersion has some effect. Thus when comparisons are made between a control and an experimental material, it is necessary to give weight to the quality index obtained on the control. The formulas thus supply a reference base to which both the experimental material and the control can be compared.

TABLE

CRACK GROWTH AND

	10 PHR replacement of EPC black						20 PHR replacement of EPC black					
			Flexing (thousands)						Flexing (thousands)			
Black	ΔT (° F)	300% modulus (lb./sq. in.)	Observed	Calculated	Quality index	Av. quality index	ΔT (° F)	300% modulus (lb./sq. in.)	Observed	Calculated	Quality index	Av. quality index
Statex-A	98	600	568	257	2.2		102	500	432	295	1.4	
	72	625	248	210	1.2		72	750	366	240	1.5	
	54	950	242	129	1.9		62	1000	266	126	2.1	
	51	1000	135	117	1.2	1.6	56	900(?)	172	138	1.2	1.5
Statex-B	90	600	372	246	1.5		85	850	415	178	2.3	
	66	750	248	178	1.4		78	975	236	148	1.6	
	60	900	236	142	1.6		54	1400	220	76	2.9	
	51	1050	218	112	1.9	1.6	44	900	188	126	1.5	2.1
Statex-93	138	550	1218	360	4.6		93	1000	530	159	3.3	
	97	1100	664	145	2.4		71	1100	294	120	2.4	
	79	1200	266	112	2.2		65	1300	212	85	2.5	
	57	1400	174	78	3.4	3.1	45	1550	117	60	1.9	2.5
Philblack	87	900	406	169	2.4		81	700	444	204	2.2	
	63	950	226	138	1.6		64	1100	222	115	1.9	
	52	1200	204	47	4.3	2.8	48	1150	116	100	1.2	1.8
Kosmos-40	106	500	460	310	1.5		85	650	505	200	2.5	
	74	700	233	195	1.2		66	1100	284	115	2.5	
	68	850	176	159	1.1		56	1250	256	93	2.7	2.6
	58	1000	195	123	1.6	1.3	—	—	—	—	—	—
Acetylene black	104	600	404	270	1.8		91	900	296	174	1.7	
	74	1000	214	138	1.5		77	1300	150	100	1.5	
	61	1200	192	100	1.9		56	1350	156	83	1.8	1.7
	50	900(?)	140	132	1.1	1.5	—	—	—	—	—	—
Gastex	93	800	481	210	2.3		93	850	498	190	2.6	
	79	900	340	159	2.1		69	900	382	148	2.6	
	60	1200	234	100	2.3		54	1000	288	120	2.4	2.5
	47	1500	136	64	2.1	2.2	—	—	—	—	—	—

* The different values given for each black represent different states of cure.

None of the compounds used in deriving these formulas contained carbon blacks other than EPC or MPC. To determine the effects of other blacks a series of compounds was made up based on the following carbon blacks in parts per hundred on the rubber:

Statex-A	50
Statex-B	50
Statex-93	50
Philblack-A	40
Acetylene black	35
Kosmos-40	40
Gastex	50

In addition, mixtures of each of these blacks with EPC were tried on the basis of replacing 10 and 20 parts of the EPC with each of them. For each black and for each mixture at least two levels for temperature build-up were secured, either by varying the time of cure or by recipe variations affecting the state of cure.

Both crack growth and hysteresis tests were run in quintuplicate from specimens cured from the same batch. Tests were run on different days over a period of several months.

The average results are given in Table IV, and the ratio of the observed life to the calculated flexing life using Equation 2 is shown.

The results given in Table IV indicate that a slight but definite improve-

IV

HYSTERESIS TESTS

Total replacement							Control, 50 PHR EPC black					
			Flexing (thousands)						Flexing (thousands)			
Parts black*	ΔT (° F)	300% modulus (lb./sq. in.)	Observed	Calculated	Quality index	Av. quality index	ΔT (° F)	300% modulus (lb./sq. in.)	Observed	Calculated	Quality index	Av. quality index
50	102	600	708	263	2.7		90	900	248	170	1.4	
	62	750	245	169	1.4		76	1000	208	140	1.5	
	61	800	336	159	2.1		44	1600	92	56	1.6	1.5
	47	1100	244	100	2.4	2.1	—	—	—	—	—	—
50	54	900	278	135	2.0	—	—	—	—	—	—	—
	55	1100	310	107	2.9	2.4	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
50	91	900	932	174	5.3	—	—	—	—	—	—	—
	44	1300	270	79	3.4	4.3	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
40	111	700	596	560	1.1		—	—	—	—	—	—
	57	1000	388	123	3.1		—	—	—	—	—	—
	38	1200	142	85	1.7	2.0	—	—	—	—	—	—
40	61	500	336	224	1.5		—	—	—	—	—	—
	61	350(?)	498	270	1.5		—	—	—	—	—	—
	39	800	214	138	1.8	1.6	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
35	81	500	398	257	1.5		—	—	—	—	—	—
	67	650	288	200	1.4		—	—	—	—	—	—
	44	950	174	120	1.4	1.4	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
50	—	—	—	—	—		—	—	—	—	—	—
	51	810	414	147	2.8		—	—	—	—	—	—
	44	950	274	121	2.2	2.5	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—

ment results from the substitution of these blacks for EPC black. Although it appears that Statex-93 gives slightly better results than the other blacks, it would be necessary to repeat the test a number of times to be certain that the improvement was beyond the experimental error of the observations.

No work has been done on compounds in which all the carbon black was replaced by an inorganic pigment. However, some data have been obtained on compounds in which varying amounts of inorganic pigments were added to the normal complement of EPC black.

The results obtained are shown in Table V. With the exception of the stock containing 15 parts of clay, the calculated flex life agrees well with the observed flex life. The exception is no doubt an illustration of the laminating or anisotropic effect described by Breckley[4]. The crack-growth results from this type of compound should be much higher than the calculated values.

Table V

Effect of Addition of Nonblack Pigments

(Basic recipe, parts by weight: GR-S 100, EPC 45, zinc oxide 5, Santocure 1.5, Turgum 10, Sulfur 2.0)

Pigment added to standard tread recipe (parts)	ΔT(° F)	Flexing (thousands) Observed	Calculated	Quality index
Control	78	170	182	0.94
Atomite whiting, 15	62	120	115	1.04
Atomite whiting, 25	76	170	195	0.87
Mica, 4	59	180	105	1.71
Clay, 7.5	61	110	112	0.98
Clay, 15	92	1110	276	4.0
Yellow iron oxide, 15	100	300	390	0.77
Soapstone, 5	79	180	186	0.97
Soapstone, 10	110	370	468	0.79

All of the data used in these derivations and illustrations were obtained on a single De Mattia type flexing machine. It was of interest to determine whether a similar relation applied to other machines.

A series of six tread compounds with varying proportions of curing agents was tested on two other machines. The first, known as the horizontal De Mattia, is similar to the one used as the standard except that it is operated at 500 cycles per minute with a stroke of 2 inches. The second was a belt-type machine not previously described in the literature, in which molded samples of $\frac{1}{4}$-inch-square cross-section, having the same transverse groove as the standard De Mattia sample, are fastened to a belt run over small diameter pulleys at a rate which gives the sample 400 flexures per minute. The results are reported as the number of cycles to produce a crack 80 per cent of the total width of the sample. In both tests twelve samples of each stock were tested on each machine.

The results are illustrated in Figure 2. The belt-type machine is about as severe as the horizontal high speed De Mattia, and both are considerably more severe than the vertical De Mattia. The slopes of the curves are approximately the same as that of the curve shown in Figure 1, which indicates that Equation 1 applies to a variety of flexing machines with a suitable revision of the constant.

The rate of crack growth in GR-S tread compounds increases rapidly with an increase in testing temperature. To determine how the curve relating crack growth to hysteresis temperature rise is shifted by an increase in testing tem-

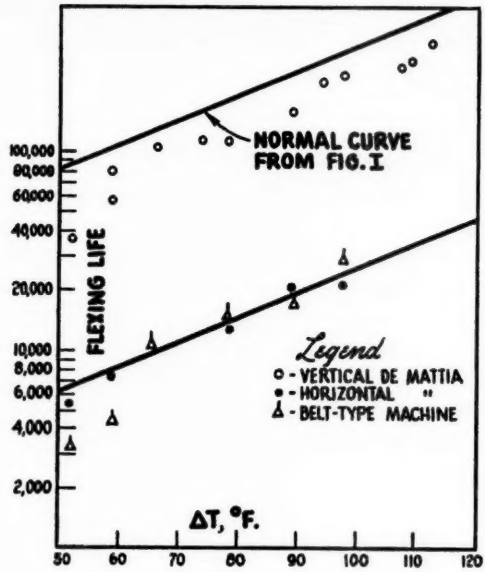

Fig. 2.—Comparison of various flexing machines.

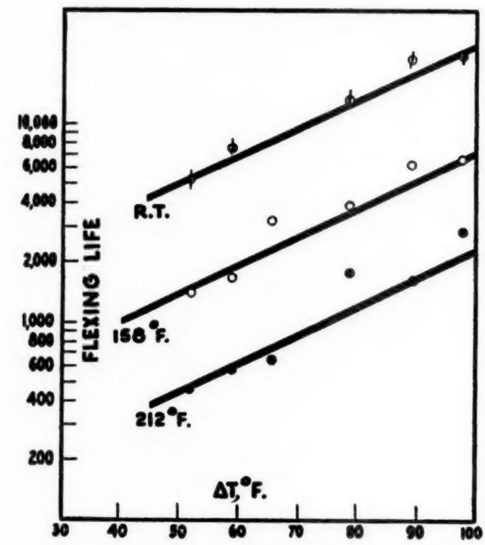

Fig. 3.—Effect of testing temperature.

perature, the six compounds used in this comparison were tested on the belt-type flexing machine at 158° and at 212° F. Figure 3 shows the results obtained at these temperatures as well as at room temperature.

One of the primary reasons for the study of this relation between crack growth and temperature rise was for the purpose of evaluating supposed im-

TABLE VI

EVALUATION OF COPOLYMERS WITH SAME TREAD-TYPE RECIPE

Charging ratio (butadiene/styrene)	Conversion (%)	Mooney viscosity (212° F, 4-min.)	Combined styrene (%)	Cure (min. at 280° F)	300% modulus (lb./sq. in.)	Tensile strength (lb./sq. in.)	Elongation (%)	Flexures	ΔT (° F)	Quality index	Average quality index
85/15	76.6	53	13.3	75	1250	3180	553	210,000–8	Blew out	—	
				150	1340	2190	447	130,000–8	77	0.73	0.73
78/22	76.7	51	21.6	75	1010	3690	661	250,000–8	98	0.76	
				150	1270	3080	513	196,000–8	70	1.4	1.1
75/25	78.3	53	24.05	75	1180	3700	606	290,000–8	92	1.1	
				150	1570	3450	527	220,000–8	65	1.8	1.5
72/28	78.5	53	27.50	75	1290	3900	607	290,000–8	91	1.1	
				150	1300	3360	527	248,000–8	66	1.9	1.5
69/31	78.2	52	29.90	75	1190	3670	622	366,000–8	88	1.5	
				150	1350	3340	518	296,000–8	63	2.5	2.0
65/35	78.8	53	33.00	60	1050	3580	620	454,000–8	91	1.7	
				150	1320	3840	567	274,000–8	59	2.6	2.2
60/40	77.5	53	37.60	75	1270	4090	661	694,000–8	82	3.3	
				150	1390	4010	620	362,000–8	61	3.2	3.3
50/50	77.6	54	47.90	75	1200	3900	593	1,552,000–8	64	9.5	
				150	1600	4000	527	604,000–8	53	6.8	8.2
X-125				75	1010	3580	700	420,000–8	103	1.1	
GR-S	—	—	—	150	910	3400	661	270,000–8	88	1.1	1.1

provements in the GR-S type of copolymer with respect to these deficiencies of GR-S, without the necessity for making precise adjustments in the testing recipe or in the state of cure. Usually only small quantities of laboratory-prepared polymers are made for preliminary evaluation purposes. Hence it is impossible to make recipe adjustments to attain the optimum sulfur and accelerator ratios or the optimum curing time without using up most of the sample.

As illustrations of the use of this procedure in the evaluation of experimental polymers, data are given in Tables VI, VII, and VIII and Figure 4 on a variety of experimental polymers.

Table VII

Evaluation of Copolymers with Chlorinated Derivatives of Styrene in Standard Recipe

Styrene derivative used	ΔT(° F)	Observed flexing (thousands)	Quality index
m-Chlorostyrene	122	2000+	3.0+
p-Chlorostyrene	81	570	2.8
o-Chlorostyrene	105	1280	3.2
	70	730	5.1
Mixed monochlorostyrenes	44	230	3.3
2,5-Dichlorostyrene	99	1450	4.2
2,4-Dichlorostyrene	85	330	1.5
	58	180	1.7
3,4-Dichlorostyrene	83	1950	9.5
2,6-Dichlorostyrene	62	110	0.9
	56	100	1.0
Trichlorostyrenes (mixed)	98	340	1.0
	64	240	2.0
Tetrachlorostyrene	65	120	1.0
	56	70	0.7

Table VIII

Evaluation of Copolymers with Vinyl Pyridine Replacing Styrene

Styrene replaced by		300% modulus (lb./sq. in.)	ΔT (° F)	Flexing (thousands) Observed	Calculated	Quality index
2-Vinylpyridine (Santocure 1.2, sulfur 1.75)		1650	70	930	63.5	14.6
		2000	57	480	39	12.3
2-Vinylpyridine (Altax 0.15, sulfur 1.6)		1150	80	1590	123	12.9
		1700	60	910	56	16.2
5-Vinyl-2-methylpyridine						
Santocure	Sulfur					
1.2	1.75	1920	57	280	42.6	6.6
		1590	58	240	62.8	3.8
1.2	1.5	2000	69	260	42.2	6.2
		1480	69	300	76.8	3.9
1.2	1.25	1010	70	290	66.6	4.4
		1510	63	280	72	3.9
1.0	1.75	—	—	—	—	—
		1850	50	430	44	9.8
0.8	1.75	1620	66	290	64	4.5
		2090	57	320	35	9.1
0.6	1.75	1740	64	290	54	5.4
		—	62	250	—	—

Table VI gives data on a series of seven copolymers in which the ratio of butadiene to styrene was varied from 85:15 to 50:50. The polymerizations were carried out very carefully, so that all had approximately the same Mooney viscosity at the normal degree of conversion used for GR-S. They were all compounded into the same tread-type recipe, and tested for crack growth and temperature rise as well as for stress-strain properties. Figure 4 shows the quality index plotted against the styrene content. Although a better quality index is obtained with higher proportions of styrene, such compositions have poorer low temperature properties than the lower styrene compositions. This illustrates the point made previously that a high quality index does not necessarily ensure the presence of other properties which are important in tire tread service.

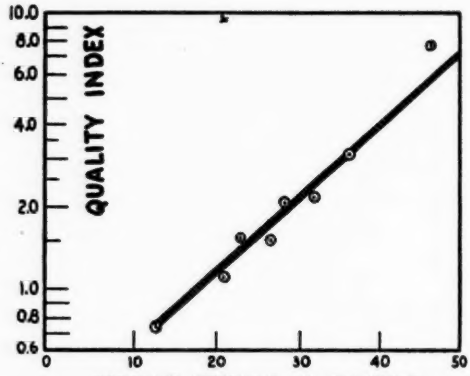

Fig. 4.—Quality index as function of styrene content.

Table VII shows results for a series of copolymers employing various chlorinated derivatives of styrene in the standard GR-S polymerization recipe. They were all compounded by the same recipe with EPC black.

In some cases an experimental polymer gives a temperature-rise value for equal modulus widely different from that obtained from GR-S. In this case Equation 2 should be used in calculating the quality index. Table VIII gives data on two copolymers in which vinyl pyridines were used in place of styrene. In this table the two values for each recipe variation represent two different cures, 75 and 150 minutes at 280° F. These data illustrate the independence of the quality index from either the time of cure or the proportion of curing agents.

Table IX shows the results obtained on tread-type stocks of natural rubber and several of the other commercially available synthetics. The first three rubbers listed, which crystallize on stretching, are considerably superior to

Table IX

Results of Tread-Type Stocks

Rubber	ΔT(° F)	Observed flexing (thousands)	Quality index
Natural	64	2000+	16+
GR-I	79	2000+	10.5+
GR-M	67	480	3.5
Hycar OR-15	87	316	1.3

GR-S; also, several of the experimental polymers shown in Table VII are superior to GR-M, one of the crystallizable rubbers. Apparently the ability to crystallize, although desirable in providing a favorable balance between temperature rise and crack growth (as well as in other properties), is not an essential requisite to the attainment of a reasonably favorable balance. (Those rubbers showing a high quality index in Table VII do not show evidence of crystallization when examined by x-ray technique.) The more favorable balance observed by certain of the experimental rubbers must be due to certain structural differences from standard GR-S, probably a greater degree of linearity.

SUMMARY

A quantitative relation has been established between rate of crack growth and temperature rise, as determined in the Goodrich flexometer test, for GR-S tread stocks compounded with normal quantities of EPC or MPC blacks. This is shown in Equation 1. The relation is valid for all variations which affect the state of cure—that is, time of cure, sulfur or accelerator variation, retarding or activating softeners, etc.

For other variations in the tread composition, such as an increase or decrease in the loading of the EPC or MPC black, Equation 2 holds. This relation is valid for all other known recipe modifications which do not involve carbon blacks other than EPC or MPC.

Improvements in the balance between flex-cracking and rise in temperature, obtained by compounding or by an improvement in the polymers, may be expressed as the ratio of the observed flexing life to the calculated flexing life using the equation appropriate to the case. This ratio is termed the quality index.

Coarser blacks substituted for the EPC or MPC blacks give an improvement in the balance between temperature rise and crack growth.

The slope of the curve relating crack growth to heat rise is the same for a variety of flexing machines and for various testing temperatures.

Knowledge of this relation has made it possible to evaluate, with some confidence, compounding changes intended to improve the resistance to crack growth without a sacrifice in temperature build-up, and also to evaluate small quantities of experimental polymers without the necessity for precise adjustments in either the proportions of curing agents or curing time.

ACKNOWLEDGMENT

The assistance of C. H. Schroeder, M. M. Goff, L. O. Schroyer, and C. T. Rood in the accumulation of the data for this study is gratefully acknowledged, as is the preparation of the varying styrene series by R. J. Houston. The polymers containing chlorinated styrenes and 5-vinyl-2-methylpyridine were prepared at the University of Illinois under the direction of C. S. Marvel. The 2-vinylpyridine copolymers were made by The Goodyear Tire and Rubber Company.

REFERENCES

[1] Breckley, *Rubber Age* (N. Y.) **63**, 331 (1943); Carlton and Reinbold, *India Rubber World* **108**, 141 (1943); Juve and Garvey, *Ind. Eng. Chem.* **36**, 212 (1944); Ludwig, Sarbach, Garvey, and Juve, *India Rubber World* **111**, 55, 180 (1944); Winn and Shelton, *Ind. Eng. Chem.* **37**, 67 (1945).
[2] Lessig, *Ind. Eng. Chem. Anal. Ed.* **9**, 582 (1937).
[3] Braendle and Wiegand, *Ing. Eng. Chem.* **36**, 724 (1944); Rupert and Gage, *Ind. Eng. Chem.* **37**, 378 (1945).
[4] Breckley, *Rubber Age* (N. Y.) **63**, 331 (1943).

MEASUREMENT OF THE SCORCH AND CURE RATE OF VULCANIZABLE MIXTURES, USING THE MOONEY PLASTOMETER *

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The rate of scorching of a vulcanizable mixture is measured by the time required for the earliest manifestations of vulcanization to appear as the result of heating at a low temperature in the range in which processing operations are carried out. The rate of curing is considered to be the time required to develop certain properties of the mixture as the result of curing at normal vulcanization temperatures. Thus the scorching time involves the early portion of the heating period (at a low temperature), while the curing rate usually involves the succeeding portion (at a high temperature). Although determinations of these rates are usually made at different temperatures, there is no good reason why both should not be determined at the same temperature if (1) a sufficiently precise method is available, and (2) if the temperature coefficients of both processes, over the temperature range involved, are known.

Many methods for measuring the scorching rate of rubber and synthetic rubber compositions have been proposed. Most of the methods depend on heating a series of samples for various time intervals and measuring the changes in certain of the physical properties. For example, Thies[1] suggested heating pellets for varying periods of time in suitable liquids and determining the time of heating required for the pellet to become insoluble in a solvent such as benzene. Similarly Twiss and Jones[2] heated pellets at three temperatures for various periods of time, and estimated the degree of cure by feeling the pellets from time to time with a rod. A common method is to cure tensile sheets for various times at low temperatures (usually in the range of 220 to 260° F) and determine the stress-strain characteristics. Nearly all the methods for measuring plasticity in rubber have been suggested at one time or another for determining scorching rate[3]. The most popular of these, judging from recent literature, is the determination of the plasticity by the Williams method[4] after various periods of heating in an air oven[5].

In 1941, Weaver[6] suggested the use of the Mooney plastometer for this purpose. He defined the scorch time as the time required for the plasticity to reach a value of 100 (on the Mooney scale), and presented data showing a close relation between this time and the curing rate at vulcanization temperatures. He recommended a temperature of 250° F as most suitable.

The determination of curing rate is most commonly done by measuring the stress-strain properties over a series of cures and noting the rate at which modulus and tensile strength develop with time of heating.

It was the purpose of the work reported here to determine whether or not measurements of both scorching rate and curing rate can be made at the same

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temperature, using the Mooney plastometer, and to determine the temperature coefficients of these two parts of the curing process over a range of temperatures which would include both processing and curing temperatures.

METHOD OF TEST

All the Mooney cure[7] tests were made on a machine equipped for steam heating and with the necessary controls so that temperatures in the range of 212 to 335° F could be attained. For temperatures lower than 212° F, an auxiliary hot water system was used. The apparatus departs from the standard machine in that the platens were modified by plugging the thermometer and regulator wells and drilling additional channels to provide steam space as near the dies as possible. No thermometers were used in the platens. Instead, special thermocouple junctions were made to replace the two plungers, and a portable potentiometer was used for taking the temperature readings of the specimen. A thermometer in the exhaust steam line was used for checking the platen temperature.

The small rotor was used in all tests reported herein to avoid excessively high torques which might have been encountered with the large rotor. Before or between tests the rotor was placed in an inverted position on the top platen to maintain its temperature as nearly as possible at the platen temperature.

All the samples were conditioned for a minimum of one week in a room maintained at 82° F and 45 per cent relative humidity. This practice was adopted because previous experience with this test had shown that it is necessary to control the moisture content of the uncured stocks if duplicable and consistent results are to be expected.

The procedure used in running a test was as follows.

The temperature of the machine was regulated to the desired level with the dies in the closed position. The temperature was checked by means of the thermocouples in the die cavity and by the thermometer in the exhaust steam line.

The samples used were in the form of $2 \times 2 \times \frac{1}{4}$-inch blocks cut from $4 \times 6 \times \frac{1}{4}$-inch slabs. A $\frac{3}{8}$-inch hole to accommodate the rotor stem was punched in one of the blocks. Duplicate tests were run at each temperature, and the averages used. If these failed to agree within 0.5-minute, a third test was made.

Two operators were required to take both the plasticity readings and the temperature readings. One operator started the test by opening the machine, quickly inserting the hot rotor through the hole in one of the samples and placing it in position in the lower die. The second sample was placed on top of the rotor, and the dies were closed. Timing was started by means of a stop watch at the instant the dies were closed. The temperature was read at this point and at 30-second intervals thereafter. After a one-minute warm-up, the rotor was started. This one-minute period is included in the total time. The initial maximum readings and the readings at each 30-second interval following are recorded. The dial reading recorded is the minimum reading in the period from 15 seconds before to 15 seconds after the specified reading time except when the plasticity is rapidly increasing. This practice eliminates the effect of needle drift.

The test was continued in each case until the plasticity value had increased at least 30 points above the minimum value observed.

A set of six compounds was made up for testing, based on natural rubber, GR-S, GR-I, and Hycar OR-15. The formulas used are given in Table 1.

TABLE 1

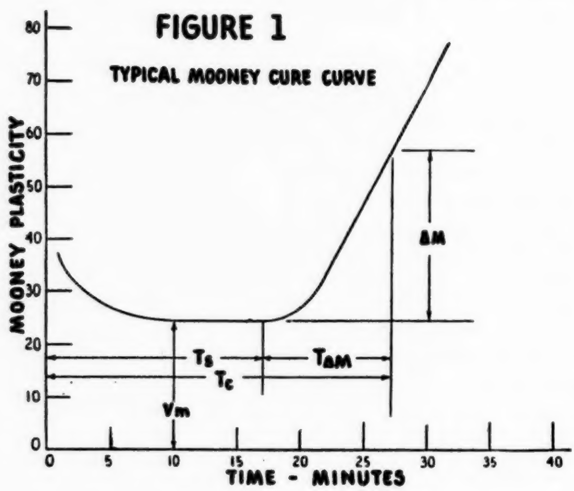
	A	B	C	D	E	F
GR-S	100	100				
Hycar OR-15			100			
Smoked sheets (No. 1)					100	100
GR-I				100		
MPC Black					50	
EPC Black		50		20		
SRF Black			100	30		
Witcarb-R*	95					
Zinc oxide (French process)	20	5	5	5	5	5
Extending resin†	10					
Stearic acid		1.5		1	2	1
Paraflux‡		5				
Bayol-D§				3		
Tarene¶					3	
Dibutyl phthalate			25			
Phenyl-beta-naphthylamine					1	1
Benzothiazyl disulfide			1			
2-Mercaptobenzothiazole	2			0.5	1	0.6
Diphenylguanidine	0.25					
Santocure‖		1.2				
Tetramethylthiuram disulfide				1		
Sulfur	3	1.75	1	2	3	3
	230.25	164.45	232	162.5	165	110.6

* Pine precipitated calcium carbonate.
† Coumarone-indene resin (m.p. 205–257° F).
‡ Petroleum softener.
§ Light mineral oil.
¶ Pine tar.
‖ *N*-Cyclohexyl-2-benzenethiazolesulfenamide.

Mooney cures were run on each compound at five or six different temperatures with approximately 10° F increments, so selected that cure would occur in a reasonable length of time at the lowest temperature.

The data for the cure of each compound at the series of temperatures used were plotted, with the temperature readings which were taken simultaneously.

A typical curve obtained at one temperature is shown in Figure 1. The



measurements which we have used herein to characterize a Mooney cure curve are the scorch point T_s (defined here as the time of the last plasticity reading which precedes a consistent rise), the plasticity at the scorch point, V_m, and the time required to reach a specified increase in plasticity over the minimum, $T\Delta_m$. The latter is used as a measure of the rate of curing.

Our reason for selecting the time of the last plasticity reading preceding a consistent rise in plasticity as the scorch point is that, immediately following this reading, the first indication of cure is manifested. The use of the time required to reach a value of 100, as suggested by Weaver[6], is objectionable for the reasons that this represents a fairly advanced state of cure and also that many of the compounds, particularly the synthetics, do not reach a value of 100, owing to slippage of the rotor or tearing of the stock. In many cases the later readings in a Mooney cure test must be discarded because of this failure.

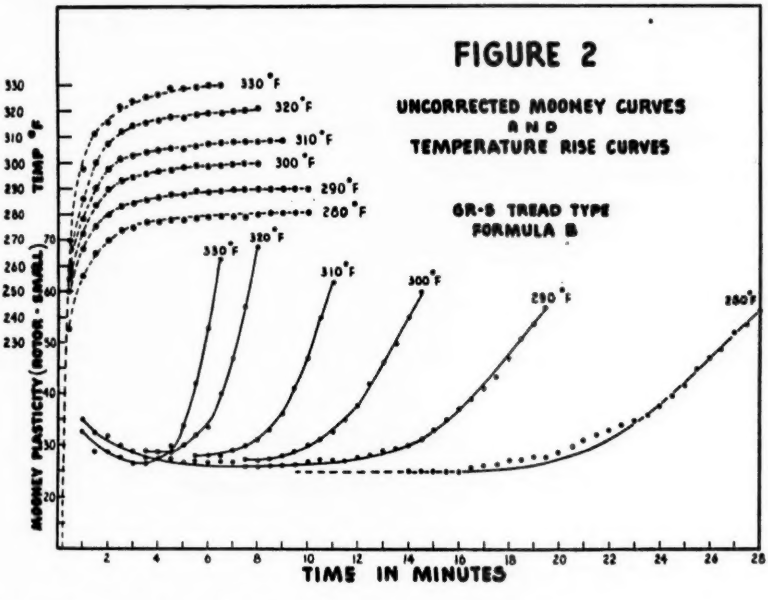
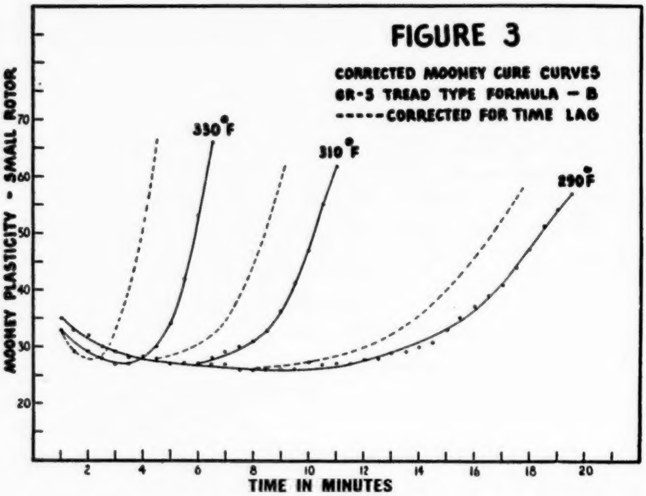


Figure 2 shows a typical set of curves for the various temperatures for the GR-S tread stock.

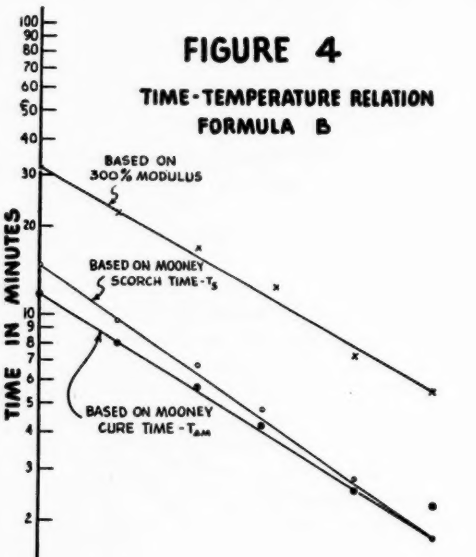
The times required to reach the scorch point or to reach a specified increase in plasticity over the minimum for a series of cures at different temperatures cannot be used directly for determining the temperature coefficients of the two processes because of the time lag in heating the sample to the impressed temperature. The curing effect obtained during the heating period is not a constant proportion of the total curing time at the different temperatures. In each case this curing effect was calculated from the temperature-rise curve on the assumption that the temperature coefficient was 2, *i.e.*, that the cure rate doubled for an increase in curing temperature of 10° C. In Figure 3, three of the curves shown in Figure 2 are replotted, along with the corrected curves obtained after this calculation.

This procedure is necessarily cumbersome, and for routine work is unnecessary. Corrections based on measurements such as these may be used for sub-



sequent tests on compounds which do not differ appreciably in thermal diffusivity, and for less precise work a fixed correction value can be used throughout. Because of the modifications made in the steam platens, the values for the correction factor, as found in this study, may be somewhat different from those with other instruments not modified in this way or which are electrically heated.

With this procedure, the scorch time and the time required to reach an additional 30 points above the minimum plasticity were scaled from the corrected curves. Both the uncorrected and corrected values are given in Table 2.



From the corrected values plotted on a logarithmic scale against temperature, the temperature coefficients were calculated. The temperature coefficient as used herein is the ratio of the time (of scorch or cure) at one temperature to the time at a temperature 18° F (10° C) higher. Typical curves for the GR-S tread stock are given in Figure 4. The values for all the stocks are given in Table 2.

Since the overall curing time is the sum of the scorch time and the cure time as defined herein, the temperature coefficient of the overall cure rate can be ob-

TABLE 2

MOONEY CURE DATA

							Temperature coefficient		
Compounds	Temp. (° F)	T_s*	T_s corrected	T_c†	T_c corrected	$T\Delta m$‡	Scorch rate	Cure rate	Overall cure rate
Formula A	190	19.5	18.3	40.0	38.8	20.5			
	198	12.5	11.4	25.5	24.4	13.0			
	210	8.5	7.2	14.6	13.3	6.1	2.3	2.3	2.3
	220	5.5	4.3	9.9	8.7	4.4			
	240	3.0	1.8	5.1	3.9	2.1			
Formula B	280	16.0	14.5	27.8	26.3	11.8			
	290	11.3	9.5	19.3	17.5	8.0			
	300	8.5	6.8	14.2	12.5	5.7			
	308	6.5	4.8	10.7	9.0	4.2	2.1	1.8	2.0
	320	4.5	2.8	7.5	5.4	2.6			
	330	3.5	1.8	6.2	4.1	2.3			
Formula C	237	22.5	20.9	39.9	38.4	17.5			
	248	14.5	12.9	25.6	24.5	11.6			
	257	8.5	6.9	17.6	16.1	9.2			
	266	6.0	4.4	15.2	13.7	9.3	2.3	1.8	2.1
	278	5.0	3.4	9.6	7.8	4.4			
	287	3.5	1.9	6.4	4.9	3.0			
	297	2.0	0.4	4.8	3.1	2.7			
Formula D	259	12.5	10.3	22.3	20.1	9.8			
	269	9.5	7.3	16.9	14.7	7.4			
	279	7.0	4.8	12.1	9.9	5.1			
	287	5.5	3.3	9.6	7.4	4.1	2.0	1.7	1.9
	297	4.0	1.8	7.2	5.0	3.2			
	305	4.0	1.8	6.1	3.9	2.1			
	316	3.0	0.8	5.2	3.0	2.2			
Formula E	247	15.0	13.0	24.5	22.5	9.5			
	256	11.3	9.3	18.0	16.0	6.7			
	270	7.0	5.0	11.6	9.1	4.1			
	275	6.0	4.0	9.9	7.9	3.9	2.1	2.0	2.0
	288	4.0	2.0	6.6	4.4	2.4			
	294	3.3	1.3	5.4	3.6	2.3			
	302	3.0	1.0	4.8	2.8	1.8			
Formula F	231	16.8	14.2	23.6	27.1	6.9			
	236	13.3	10.7	20.1	17.6	6.9			
	249	8.8	6.2	13.4	10.9	4.7			
	257	6.5	3.9	10.5	7.8	3.9	2.4	1.4	1.9
	266	5.0	2.2	8.8	6.3	4.1			
	277	4.0	1.4	6.9	4.1	2.7			
	282	3.8	1.3	6.0	3.3	2.0			

* Time to reach scorch point.
† Time to reach cure point (30 points above minimum viscosity).
‡ Time between scorch point and cure point (corrected).

tained by combining these times and plotting, as above, against temperature. This value is also given in Table 2.

Because of the possible sources of error in calculating the curing effect which occurs during the heating to the impressed temperature, it was considered desirable to check the Mooney procedure by a more conventional method. For this purpose thin press-cured sheets were prepared from several of the compounds used, in a manner which reduced the possible error due to time lag to an insignificant value. This was done by the following method:

The stock was calendered 0.030-inch thick on aluminum sheet 0.012-inch thick. After conditioning the stock to constant humidity a second sheet of aluminum was rolled on to the other side. The samples thus prepared were cut 3.5 × 7 inches. An 8 × 8-inch steam-heated press, which had been carefully checked for temperature control and distribution, was used for curing. separator 8 × 8 × 0.05 inch was made with a section cut out on one side to accommodate the 3.5 × 7-inch plied sample. This was placed in the press with the opening toward the front of the press, and the press was closed. After the required temperature had been attained in the press platens, the press was opened just enough to permit insertion of the sample and was immediately closed. A stop-watch was started when the press was closed. At the end of the cure the sample was removed and dropped into a pail of ice-water. Thermocouple measurements showed that the sample attained the impressed temperature in approximately ten seconds. Cures were chosen at each temperature, starting at the shortest time that would give a measurable modulus, and with all the time intervals on the rapidly rising part of the modulus time curve. Six temperatures at 10° F increments were chosen. As many tensile specimens as the condition of the sample permitted (using a small die $\frac{3}{4}$-inch bench marks on a $\frac{1}{8}$-inch wide restriction section) were cut from each sheet and pulled on a 60-pound capacity Scott machine. After rejection of bad breaks, the remaining values were averaged, and the modulus values plotted *vs.* time of cure.

From the modulus-time curves so obtained the times required to reach a specific value of modulus at the different temperatures were scaled, and are shown in Table 3, with the temperature coefficients obtained from curves of log time against temperature. The data for the GR-S tread stock are shown in Figure 4. Since the times involved in this measurement include the scorch

TABLE 3

Formula A

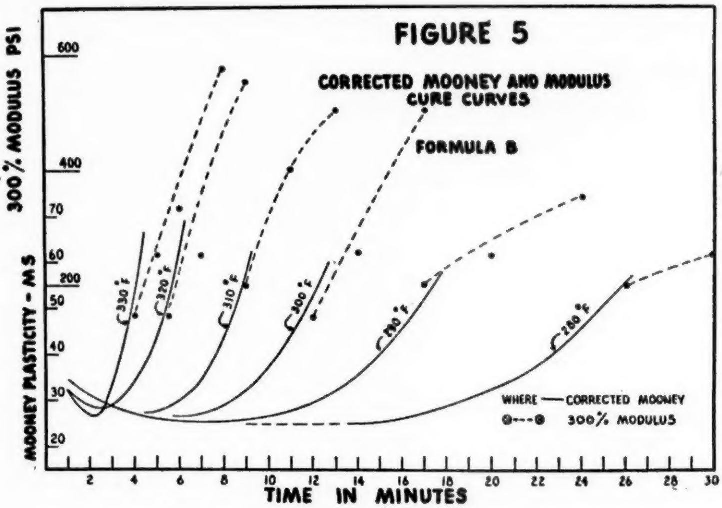
Temperature ° F	Time of modulus of 800 lbs. per sq. in. min.	Coefficient
230	33.3	1.9
240	27.2	
250	15	
260	12.5	
270	7.8	
280	6.5	

Formula B

Temperature ° F	Time of modulus of 800 lbs. per sq. in. min.	Coefficient
280	32.0	1.9
290	22.5	
300	17.0	
310	10.3	
320	7.4	
330	5.8	

time, the temperature coefficients obtained should check the overall coefficients obtained from the Mooney data. The results show that the agreement is excellent, and indicate that the corrections for time lag in heating the Mooney specimen to the impressed temperature were correct and that the Mooney method is satisfactory for measurements of this kind.

The validity of the use of that portion of the Mooney cure curve following the scorch point as a measure of the curing rate might be questioned. While rate of cure measurements are usually based on the rate of change of stress-strain properties, there is no reason why any other property which is altered by the vulcanization process could not be used. That the change in plasticity during the period following the scorch point approximately parallels the change in modulus is demonstrated by the curves in Figure 5. In these curves the



modulus data obtained by the procedure described above for the GR-S tread stock have been plotted on the same time scale as the corrected Mooney curves. It is of interest to note that for this particular compound the earliest measurable degree of cure in the press-cured sheets corresponds to a Mooney value (small rotor) of about 50.

SUMMARY AND CONCLUSIONS

The Mooney plastometer may be used to measure the scorching rate and the curing rate of vulcanizable mixtures through a range of temperatures, including the usual processing and curing temperatures. From the data obtained the temperature coefficients of the two processes can be readily calculated. The values for the latter, for the particular mixtures tested, were as follows:

Formula	Scorch rate coefficient	Cure-rate coefficient	Overall cure-rate coefficient
A	2.3	2.3	2.3
B	2.1	1.8	2.0
C	2.3	1.8	2.1
D	2.0	1.7	1.9
E	2.1	2.0	2.0
F	2.4	1.4	1.9

The combined cure-rate coefficients should correspond to those determined from stress-strain data. These were found to be:

	Cure-rate coefficient	
Formula	From Mooney data	From stress-strain data
B	2.0	1.9
F	1.9	1.9

This agreement confirms the accuracy of the corrections applied to the Mooney data as well as the Mooney method for these measurements.

When the scorch and cure-rate coefficients are known, both rates may be measured at one temperature, and the results obtained extrapolated with some confidence to higher or lower temperatures.

REFERENCES

[1] Thies, *Ind. Eng. Chem.* **20**, 1223 (1928).
[2] Twiss and Jones, *J. Soc. Chem. Ind.* **54**, No. 3, 13T (1935).
[3] Marzetti, *India-Rubber J.* **66**, 417 (1923); Williams, *Ind. Eng. Chem.* **16**, 362 (1924); Dieterich and Davies, *Ind. Eng. Chem. Anal. Ed.* **3**, 297 (1931).
[4] Odenwald and Baader, *Proc. Rubber Tech. Conf. London*, **1938**, p. 347.
[5] Krall, *Ind. Eng. Chem.* **16**, 922 (1924); Morley, Scott and Willott, *J. Rubber Research* **13**, 164 (1944); Rubber Chem. Tech. **18**, 460 (1945).
[6] Weaver, *Rubber Age* (N. Y.) **48**, 89 (1940); Rubber Chem. Tech. **14**, 458 (1941).
[7] Since the degree of cure attained at the end of a typical test is well beyond the "scorch" stage, we prefer the term "Mooney cure" rather than "Mooney scorch" for the test.

THE COEFFICIENTS OF ADHESION OF RUBBER *

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INTRODUCTION

Of all the physical properties characteristic of rubber there seem to be few which have received less attention up to the present time than its coefficients of adhesion to other materials. Yet this is a problem which is of importance both from the technical and from the scientific point of view, and which is of concern in such uses of rubber as in pneumatic tires and belts, to mention only two highly important applications.

In the systematic study which was undertaken by the author, it was attempted to operate under conditions which could be easily reproduced; furthermore it was considered to be preferable to use samples of rubber prepared in the laboratory rather than sections of tires or of belts, as have been used for the most part by earlier investigators who have worked on this problem.

From the results obtained in the present investigation it is possible to derive various general laws which are applicable to well defined conditions of contact and of condition of surface. In actual service there are other factors to be taken into account which are not involved in the present work. Nevertheless, the theoretical principles which have been established should be of aid in the work of technologists who are interested in the frictional properties of rubber because these principles furnish a means for judging the relative importance of the various factors involved.

DEFINITIONS OF COEFFICIENTS OF ADHESION AND OF FRICTION THE LAWS OF COULOMB

The reciprocal friction between the contact surfaces of solid bodies can be conveniently characterized by a numerical value which represents the ratio of the tangential force which causes sliding on each other to the normal force which compresses one against the other. This value, which is designated as the *coefficient of friction*, can also be considered as the trigonometric tangent of the angle formed by the resultant of the forces of contact and by the normal to the plane of separation of the rubbing surfaces.

From a more precise point of view, two factors should be distinguished:

(1) the *coefficient of adhesion* or *coefficient of static friction*, which is a measure of the force necessary to overcome the friction after a certain time of rest, and

(2) the *coefficient of dynamic or kinetic friction*, which measures the force necessary to overcome the friction when the velocity of slipping has a constant finite value.

The first scientific investigation must be credited to Leonardo da Vinci, who, about 1500 A.D., studied friction by placing solid bodies on planes in-

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clined at different angles. One hundred and fifty years later, Amoutons formulated the first laws of friction for solid bodies. These essentially empirical laws are known by the name of the laws of Coulomb[1], and can be summed up by the following three propositions:

(1) the frictional force is proportional to the normal force;
(2) the frictional force is independent of the area of the surfaces of contact;
(3) with metals, the frictional force is independent of the velocity.

With the exception of some work published by Roth, Driscoll, and Holt[2], there has been hardly any study of the coefficients of adhesion and friction other than studies of manufactured products with a view to obtaining technical information. But in spite of their lack of precision, these tests make evident one important theoretical point, *viz.*, that the ordinary laws of friction are not valid for rubber, whose coefficient of friction increases with decrease in the contact pressure, or with increase in the velocity of slipping[3].

Previous investigators have shown also that rubber is a material which is capable of developing, even without being subjected to any unusual conditions, coefficients of friction so high as to be close to unity on the surfaces of solid bodies. Furthermore, whereas the coefficients of friction of solid bodies are practically independent of the pressure, velocity, and temperature, the coefficients of rubber are sensitive to variations in these three factors.

The question therefore arises as to what are the laws which govern these changes in the coefficient of friction of rubber, and how to interpret this novel characteristic of a material whose physical properties are still not well understood. Precise experimental data have been lacking in answer to these questions, the solution of which has awaited the development of suitable apparatus and technique.

DESCRIPTION OF THE TESTING EQUIPMENT

The experience of previous investigators and experiments carried out by the present author with improvised types of apparatus have shown above all else the necessity of developing an apparatus which is especially adapted to studying rubber.

The principle of the *frictiometer* finally adopted (see Figure 1) is based on the precise determination of the maximum of the angle α formed by the resultant of the contact forces between the track and sample and the normal to the interfacial plane.

The essential part of the apparatus (see Figure 2) is a rigid block of triangular form MON, which is articulated at its lower part around the axis O of the support for the rubber sample B placed on the track A, which remains immovable during the measurements. The head M of this beam rests without friction, because of a roller bearing placed in M, against a vertical wall V. Starting from point N, a heavy carriage moves, by the action of a counterweight, slowly toward M by rolling in the horizontal rail MN.

As long as the carriage does not go beyond a certain limiting position, the forces of adhesion exceed the tangential force resulting from the couple which tends to swing the beam and oppose all relative displacement between the surface of the track and that of the sample on it. The beam therefore remains immovable when the sample A is sufficiently rigid not to undergo any deformation in the tangential sense.

From the viewpoint of mechanics, this state of equilibrium can be expressed by the possibility of applying the parallelogram rule to the three contributing forces which act at this moment on the beam:

(1) the vertical force *P* exerted at point *C* by the weight of the carriage;
(2) the horizontal reaction *H* of the vertical wall *V* on the head of the beam;
(3) the reaction *R* of the track in sliding on the sample.

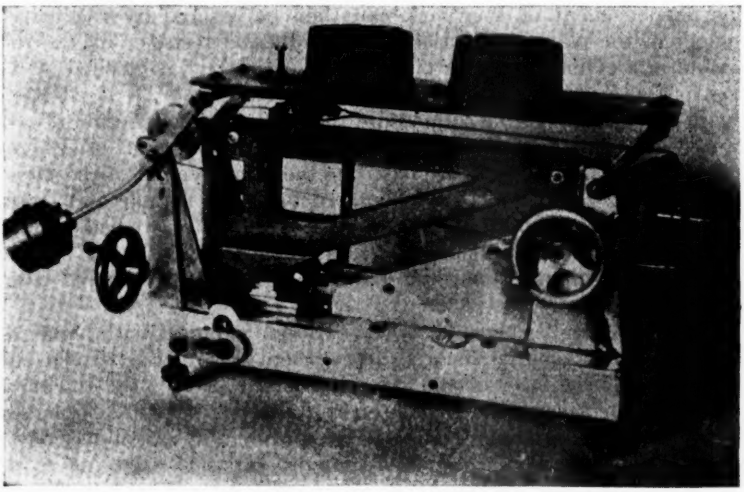

FIG. 1.—Photograph of the frictiometer (side view).

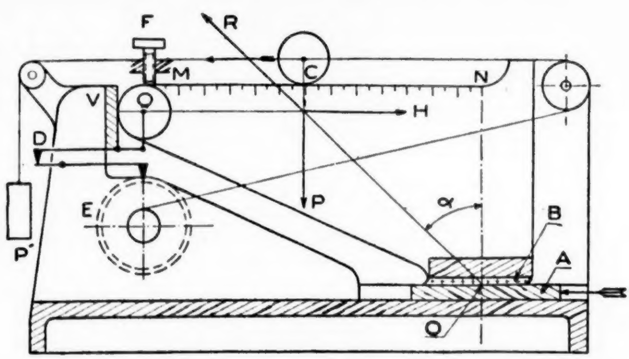

FIG. 2.—Diagrammatic view showing the principle of the frictiometer.

It is evident that the direction of this last force is determined at any particular instant by the position of the carriage on the rail. A state of equilibrium continues until the angle α reaches a critical value at which sliding commences. The horizontal displacement, which is very slow, of the rubber sample on the track, is accompanied by a vertical fall 2.5 times as great as that of the head of the beam, the movement of which is itself amplified 50 times by a double lever system *D*. A pawl attached to the end of the second lever engages itself in

the notch of a wheel E, the rotation of which is governed by the displacement of carriage C. The sensitivity of the system is sufficiently great so that sliding of the order of 0.01 mm. is capable of automatically stopping the progress of the carriage along the rail. From the position at which the carriage stops it is possible to determine readily the coefficient of friction by the relation: $f = \tan \alpha$.

The apparatus can be operated in the same way when it is desired to measure the coefficient of kinetic friction instead of the coefficient of adhesion. The relative displacement of the track can then be assured by the translatory movement of the plane track used for the adhesion tests, or by the rotatory movement of a cylindrical track of highly polished steel, controlled by a speed reducer located at the back part of the apparatus.

In this way it is possible to measure the coefficients of friction of ordinary solids by the same standards as with other forms of apparatus used heretofore for this sort of test, and which are based on the measurement of the slope of an inclined plane or the tractive force required to slide a sample on a horizontal plane. On the other hand these earlier types of apparatus are badly adapted to the measurement of the coefficients of friction of rubber for, with rubber, two fundamental difficulties are encountered which are not encountered with ordinary solid bodies.

If a sample of rubber placed between two rigid supports with plane surfaces is subjected to a tangential shearing force, there is a relative displacement of the upper and lower faces of the sample, and the greater the thickness, the greater is this displacement. This pseudo-sliding normally takes place simultaneously with true sliding, and reduces considerably the precision of the measurements. It can be eliminated only by carefully adhering to a rigid support a thin sample of rubber which is already deformed to its maximum in a tangential direction. This condition can be readily obtained with the new apparatus described in the present work by sliding the sample a certain distance before making the measurements.

The extreme slowness in the sliding of the surfaces of the rubber on the solids also deserves special comment. Whereas the spontaneous sliding of rigid solids on a plane inclined to a progressively greater degree represents the sudden upset of a stable equilibrium, the sliding of rubber is, on the contrary, the inappreciable passage from complete adhesion to complete release from the adhesion through a whole series of intermediate states of equilibrium, during which the sample of rubber is displaced on the track at a constant velocity which does not at the beginning exceed one micron per second. This sort of creep resembles the slow deformations or flow of a plastic mass subjected to mechanical forces. Since it is the initiation and changes in velocity of this slow sliding which determine the critical values of the tangential force, it is necessary, in order to obtain precise results, to have available an amplifying device and a sufficiently sensitive automatic release.

CONDITIONS FOR REPRODUCIBILITY

The construction of a special testing apparatus does not entirely solve the problem, and reproducible results can be obtained only after the development of a suitable experimental technique for preparing the track and samples.

After various trials and numerous tests which were unsuccessful, a simple procedure was adopted, which fulfilled the following three conditions, all of which are of fundamental importance.

(1) the perfect attachment of the rubber sample on a rigid support;
(2) a definite surface of contact and a strictly uniform pressure of contact between the track and smooth surface of the rubber, and
(3) the absence of all moisture on the contact surfaces.

After having made sure that these precautions are strictly observed, the friction tests can be made, but these too must be carried out in a methodical way. It was found, in fact, in agreement with Roth, Driscoll, and Holt[2], that there is apparently a change in the friction forces at the beginning of the sliding, for the coefficient of adhesion increases from 15 to 20 per cent during the first four or five successive tests, and then reaches a constant limiting value which can be accepted as the characteristic value of the coefficient of adhesion for the particular contact pressure involved.

The reproducibility of the values obtained for this limiting coefficient, when the same test is repeated with various samples prepared in the same way, is of the order of 2 per cent, even when no special precautions are taken about the plasticity of the unvulcanized mixtures.

The thickness of the vulcanized rubber sample is a more important factor than is the plasticity of the unvulcanized mixture. It apparently has no direct effect on the coefficients, but above 2–3 mm., it tends to facilitate pseudo-sliding, and the results obtained are then too low.

With samples which are too thin, it becomes very difficult to obtain good contact between the rubber and track. A thickness of 1 mm. represents a very good compromise.

Other experimental factors influence the coefficients of adhesion and friction of rubber. These may be briefly reviewed, beginning with those which depend on the experimental conditions, and are independent of the nature of the rubber sample.

A STUDY OF EXTRANEOUS FACTORS

INFLUENCE OF THE PRESSURE AND OF THE SURFACE OF CONTACT

The pressure and the surface area of contact are two factors which cannot be studied separately, because the pressure is equal to the quotient, of the vertical load and the actual area of contact. These two factors, moreover, vary simultaneously when the materials in contact are rigid bodies, and their exact values are impossible to determine.

This is not true of rubber, which is an easily deformable material, and the surface of which actually in contact with another material does not depend on the external force which compresses the two bodies together when contact is perfect.

The coefficients of adhesion of soft rubber decrease considerably with increase in pressure. The order of magnitude for a vulcanizate of the pure-gum type in contact with a track of smooth glass at 18° C is 2 at a pressure of 2 kg. per sq. cm. and 1 for a pressure of 10 kg. per sq. cm. On the contrary, at constant pressure, the coefficients of adhesion of rubber are independent of the area of contact; the tangential force of adhesion is, therefore, directly proportional to this area of contact.

If a graph is made from data obtained on samples tested under the same experimental conditions except for different areas of surface contact, with the ordinate representing the limiting coefficients of adhesion A_1 and the abscissa the pressures of contact P (see Figure 3), it will be found that the plotted points fall on a single hyperbola.

It is more convenient to replace the limiting coefficient of adhesion A_1 by its reciprocal $1/A_1$, which can be regarded as the coefficient of sliding of the bodies in contact with each other. There is thus obtained, as a function of the contact pressure, a straight line AB, which passes above the origin of the coördinates. However, if the contact pressure falls below 3 kg. per sq. cm., the plotted points follow a curve which, at first tangent to the straight line AB, approaches more and more rapidly the pressure abscissa and finally passes through the origin.

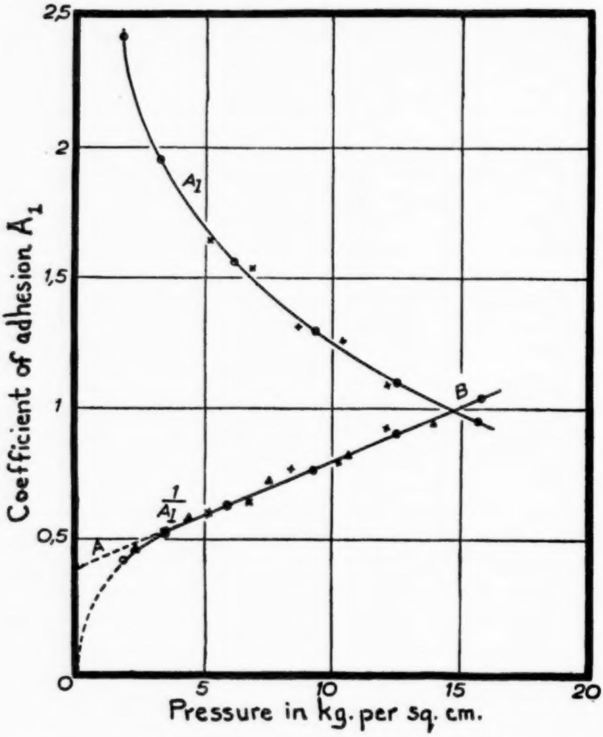

FIG. 3.—Influence of the area of contact and of the pressure on the coefficient of adhesion A_1 of rubber (pure-gum type of mixture).
Sample 1 mm. thick on glass track at temperature of 18 C.
○○○ area of contact 1.62 sq. cm. metal support.
××× area of contact 2.90 sq. cm. metal support.
▲▲▲ area of contact 1.29 sq. cm. belt support.

Hence the coefficient of adhesion of soft rubber tends toward an infinite value as the contact pressure approaches zero. It is probable that this anomaly is the result of the combined effects of atmospheric pressure and true adhesion. It was verified experimentally that there is still true adhesion between rubber and solid bodies when the tests are carried out in a vacuum and that it has high values, *i.e.*, of the order of 300 grams per sq. cm. for vulcanizates of the pure-gum type and as high as 1 kilogram per sq. cm. for vulcanizates containing high proportions of mineral fillers, such as magnesium carbonate.

This adhesion is of secondary importance compared with the linear relation between the limiting coefficient of sliding, *i.e.*, the reciprocal of the coefficient

of adhesion of rubber on solid surfaces, and the contact pressure when the latter varies between 3 and 20 kg. per sq. cm. The coefficients of adhesion of rubber can be characterized by extrapolating this relation toward high and low contact pressures by only two values: the ordinate at the origin, c, and the slope b of the straight line AB represented by the equation:

$$\frac{1}{A_1} = bP + c$$

The first of these parameters is none other than the reciprocal of the maximum coefficient of adhesion at zero pressure, provided it is assumed that the linear relation still holds true for low contact pressures. As for the second parameter, it can be readily demonstrated that it represents the reciprocal of the maximum tangential force per unit of surface area of contact, the pressure then being infinite.

INFLUENCE OF THE VELOCITY OF SLIDING

The third law of Coulomb relates to the influence of the rate of sliding. Here again the behavior of rubber is singularly different from that of ordinary solid bodies. With these latter, the coefficients of friction are never greater than the coefficient of adhesion. On the other hand, in the case of rubber, considerable increases in the coefficients are observed when the velocity of sliding increases from zero to 1 cm. per second; in other words, as with the abrasion, vibration and heating do not play any part.

INFLUENCE OF THE TEMPERATURE

The physical properties of rubber change considerably, even after vulcanization, with change in the temperature of testing. Its coefficients of adhesion are no exception to this rule, and they decrease greatly with increase in temperature. The curves of the coefficient of sliding as a function of the pressure form a system of straight lines spreading out in fanlike formation, while the maximum coefficient of adhesion remains virtually constant.

Figure 4 shows curves characteristic of a vulcanizate of the pure-gum type on glass at the prevailing temperature (18° C) and at 50° C. It is evident that to compare the influence of other experimental factors on the adhesion of rubber, it is indispensable to operate at exactly the same temperature.

TABLE 1

INFLUENCE OF THE VELOCITY OF SLIDING ON THE COEFFICIENTS OF FRICTION OF VULCANIZED RUBBER

(Pure-gum vulcanizate on glass track at 18° C)

Pressure	Velocity (mm. per sec.)		
(kg. per sq. cm.)	0	0.08	0.2
4.6	1.46	1.63	1.76
13.8	0.75	1.10	1.20

INFLUENCE OF MOISTURE ON THE SURFACES

The influence of moisture on the coefficients of adhesion of rubber is no less great than that of temperature. Furthermore, the lubricating action of a film of water on rubber has been put to use, with great success, for bearings with rubber linings, which operate with coefficients of friction of the order of 0.02.

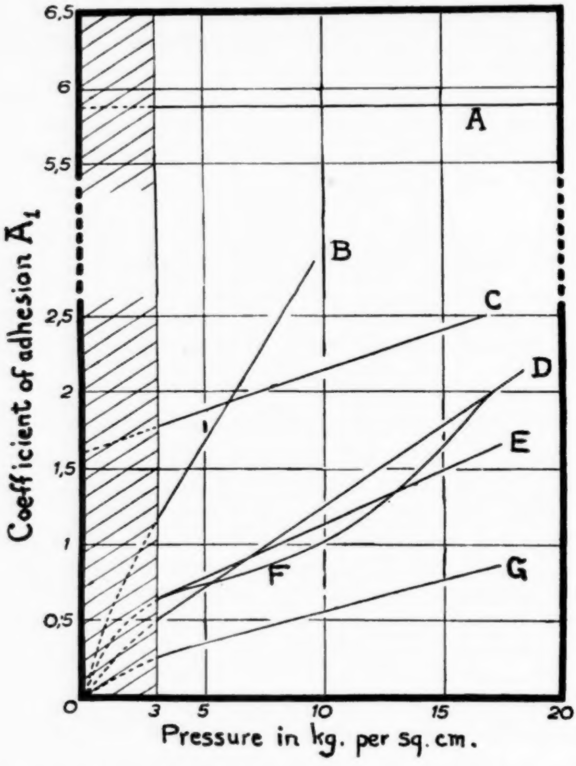

FIG. 4.—Influence of the principal factors on the coefficient of adhesion A_1 of rubber.
Curve A Ebonite on glass.
Curve B Vulcanized loaded rubber mixture on glass at 50° C.
Curve C Frozen loaded rubber mixture on glass.
Curve D Raw rubber on glass.
Curve E Vulcanized loaded rubber mixture on glass.
Curve F Rubber on rubber.
Curve G Loaded rubber mixture on glass.

It is perhaps more surprising to find that the coefficients of adhesion require more than a week to revert to their original values if the liquid evaporates under normal conditions, although the surface of the rubber is apparently absolutely dry. The increase in the coefficients is much more rapid when evaporation takes place in a vacuum bell jar or when the rubber is compressed against a solid surface.

INFLUENCE OF THE NATURE AND CONDITION OF THE SURFACE OF THE TRACK

In a general way, changes in the character of the track do not change the results greatly; the changes which were observed were of the order of 10 per cent. When compared with that of rubber on metals, the resistance of rubber to sliding on glass is relatively high; on ebonite it is relatively low.

Rubber tracks differ notably from tracks of rigid materials; the critical sliding value of rubber is not a linear function of pressure, for the decrease in the coefficient is disproportionately rapid with increase in pressure (see Figure

4). Apparently there is still greater deviation from the law of Coulomb than with contact between rubber and a rigid solid.

The influence of roughness of the surface of the tank on the coefficient of adhesion of rubber would seem at first view to be rather paradoxical, since such roughness reduces notably the resistance to sliding, whereas ordinary experience with contact of rigid solid to rigid solid has led to diametrically opposite results. However, other authors have called attention to this fact[4], and it should be pointed out also that the roughness in this case does not tend, as it were, to imbed itself in the rubber and thus to form snags mechanically. Under these conditions a rough surface has a tendency merely to decrease the effective surface area of contact and to set up excess pressure at local spots. These two effects are manifest in a decrease in the coefficient of adhesion.

STUDY OF FACTORS ON WHICH THE STATE OF THE RUBBER DEPENDS

INFLUENCE OF THE CONDITIONS OF VULCANIZATION

With increase in the state of vulcanization, the maximum value of the coefficient of adhesion decreases; *e.g.*, the coefficients of adhesion at ordinary contact pressures are much smaller for ebonite than for soft rubber (see Figure 4). On the other hand, the maximum tangential force increases with increase in the state of cure and becomes infinite in the case of ebonite, which shows a characteristic horizontal line. Hence, unlike soft rubber, ebonite conforms to the law of Coulomb, since its coefficients of friction are independent of the pressure and of the surface area of contact.

When various accelerators are used to vulcanize mixtures of the pure-gum type and when the time of heating is prolonged, the same results are obtained. The greater the activity of the accelerator or the longer the time of heating, the greater is the maximum tangential force (see Table 2). There is no exception to this rule, except when sulfur bloom has an influence on the phenomenon.

TABLE 2

INFLUENCE OF THE TIME OF VULCANIZATION ON THE ADHESION CHARACTERISTICS OF A PURE-GUM VULCANIZATE

(Diphenylguanidine and mercaptobenzothiazole as accelerators; temperature 18° C; glass track)

	Time of heating (in minutes)			
Adhesion factor	0 (raw)	5	10	30
Maximum tangential force (kg. per sq. cm.)	12.5	21.8	28.6	34.5
Maximum coefficient of adhesion	3	2.56	2.30	1.96

INFLUENCE OF THE LOADING OF MINERAL FILLER

The physical properties of soft rubber are changed as notably by the presence of mineral fillers as by changes in the vulcanizing conditions. This is true also of the coefficients of adhesion of vulcanizates, which are increased considerably by the presence of fillers, such as magnesium carbonate (see Figure 4).

INFLUENCE OF FREEZING, STRETCHING, AND AGING

When raw rubber is kept at a sufficiently low temperature, it crystallizes, and this change seems to have a certain repercussion on its coefficient of adhesion. A comparison of the results obtained with a sample of smoked sheet

at 18° C (see Figure 4) with the results obtained with the same sample which is thawed progressively (decrease in Shore hardness from 88 to 35) indicates that the rubber gel acts in the same way as does vulcanized rubber, *i.e.*, the slopes of the characteristic straight lines decrease, and they meet the ordinate at higher points.

Natural rubber is likewise crystallized by simple stretching. No relation was, however, found, even before vulcanization, between its adhesion characteristics and its degree of stretching, probably because of the impossibility of attaching the samples satisfactorily on their supports[5].

All the tests so far described were carried out with freshly prepared samples, but the properties of rubber change as time goes on through aging resulting from autoxidation. This aging process can be considerably accelerated, for example, by heating in an oven at 70° C. When vulcanized rubber undergoes accelerated aging in this way, its coefficients of adhesion are reduced considerably; the presence of an antioxidizing agent retards, as might be expected, these changes. On aging, the maximum tangential force decreases at first, but when the vulcanizate has hardened to such an extent that it is no longer rubbery and elastic, it then behaves like ebonite and conforms to the law of Coulomb.

STUDY OF THIOKOL AND POLYVINYL CHLORIDE

Tests carried out with Buna[6], as well as with Thiokol and polyvinyl chloride, indicate that the results obtained with rubber apply equally to other materials of the same type, such as synthetic elastomers and synthetic resins with rubberlike properties. Thus, like rubber, Thiokol and polyvinyl chloride show linear relations between sliding and contact pressure.

However, the corresponding maximum tangential forces are smaller than those of natural rubber, whose coefficients of adhesion are higher at any given temperature.

CONCLUSIONS

What conclusions can be drawn from all these experiments? Attempts to find a possible relation between the adhesion characteristics and other mechanical properties of rubber have been unsuccessful. Nevertheless, from a purely qualitative point of view alone, the coefficients of adhesion become progressively less sensitive to pressure as the rubber approaches more and more to the solid state[7]. This seems to be a general rule to which there is no exception.

The theoretical interpretation of this peculiar property of rubber cannot be discussed within the scope of the present paper; in fact it offers a complicated problem, for scientific data on the behavior of rigid solids in contact are extremely scarce. Theories advanced to explain the external friction of solids are numerous, but none gives a truly complete explanation of the phenomenon. However, it seems probable at least that the peculiar behavior is attributable to the characteristic state of materials with rubberlike properties, *i.e.*, a state intermediate between that of liquids and of solids.

There are numerous applications where advantage is taken of the high resistance to sliding of rubber on the surfaces of dry solid bodies. There would be no point in calculating *a priori* their coefficients of adhesion under service conditions from the results obtained in the present work, for conditions in service are generally of a very complex nature and, also are extremely variable. Pneumatic tires on automobiles are a very good example of such conditions.

On the other hand, in applications such as transmission belts and autorail pneumatic tires, which operate under much more uniform conditions, there is reason for believing that systematic tests of this kind might be of some use.

ACKNOWLEDGMENT

The author takes this opportunity to express his deep gratitude to E. Darmois, Professor on the Faculty of Sciences, and to Jean Le Bras, who have been so good as to follow and guide the progress of this investigation, and also to thank the French Rubber Institute.

REFERENCES

[1] Coulomb, "Théorie des machines simple", Paris, **1821**.
[2] Roth, Driscoll, and Holt, *J. Research Natl. Bur. Standards* **28**, 439 (1942).
[3] Vogt, *Ind. Eng. Chem.* **20**, 302 (1928); Breuil, *Caoutchouc & gutta-percha* **26**, 14, 405 (1929); Derieux, *J. Elisha Mitchell Scient. Soc.* **50**, 53 (1934); Rubber Chem. Tech. **8**, 441 (1935).
[4] Ariano, *India-Rubber J.* **78**, 351 (1929); 56 (1930); Roth, Driscoll and Holt, *J. Research Natl. Bur. Standards* **28**, 439 (1942).
[5] Sliding must take place in a direction perpendicular to the stretching, for the abrasion is extremely great when the friction is in the same direction as the stretching.
[6] These tests were carried out by the Société Coulombes Goodrich.
[7] Le Bras and Thirion, *Compt. rend.* **220**, 812 (1945).

PRECISION OF TESTS FOR TEAR RESISTANCE *

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The Winkelmann tear test with the crescent specimen has been widely used in the rubber industry. The American Society for Testing Materials[1] has adopted this test, using two forms of the crescent specimen, with a single nick in each as recommended by Poules[2].

Recently Buist[3] demonstrated that the result obtained with the A.S.T.M. type B crescent specimen is very sensitive to the depth of the nick. He found that the same blade-setting did not make the same depth of nick in all stocks. To overcome this difficulty he developed a cutting machine in which the blade setting could be changed to secure, by cut and try, a nick depth of exactly 0.02 inch, as specified by the American Society for Testing Materials.

Just previous to the publication of Buist's work, a paper by Graves[4] described tests on an angle-tear specimen, and gave data and observations to show that this specimen had the following advantages over the crescent specimen:

1. No nick is required.
2. Test results are more reproducible.
3. Pulling stress is more concentrated at the point of rupture.

The present authors desired to check the better precision (reproducibility) claimed for the test with the angle specimen, since this feature has the most interest to testing laboratories. An increase in the precision of the test enables smaller differences in tear resistance between stocks to be recognized, and reduces the number of specimens which must be tested to secure a reliable average value for any stock.

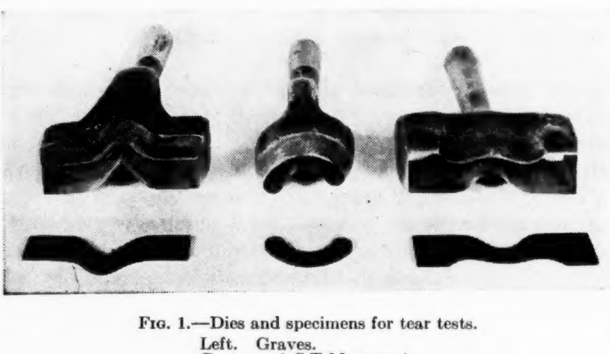

Fig. 1.—Dies and specimens for tear tests.
Left. Graves.
Center. A.S.T.M. type A.
Right. A.S.T.M. type B.

* Reprinted from *Analytical Chemistry*, Vol. 19, No. 7, pages 436–438, July 1947. The present address of the second author, R. U. Bonnar, is Shell Development Co., Emeryville, California.

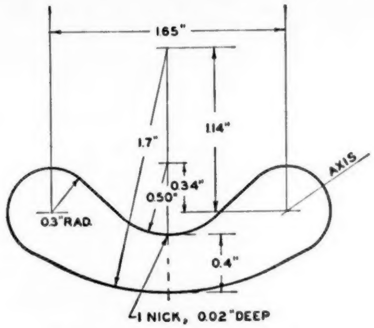

FIG. 2.—A.S.T.M. type A specimen.

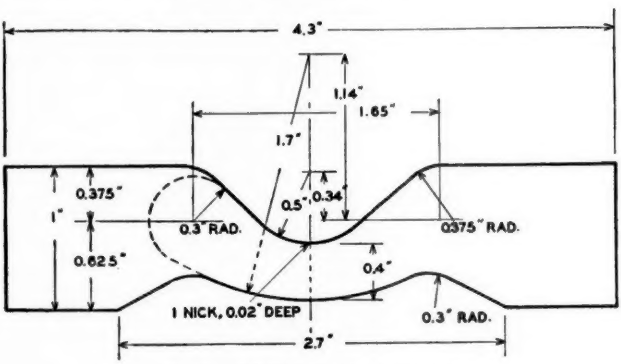

FIG. 3.—A.S.T.M. type B specimen.

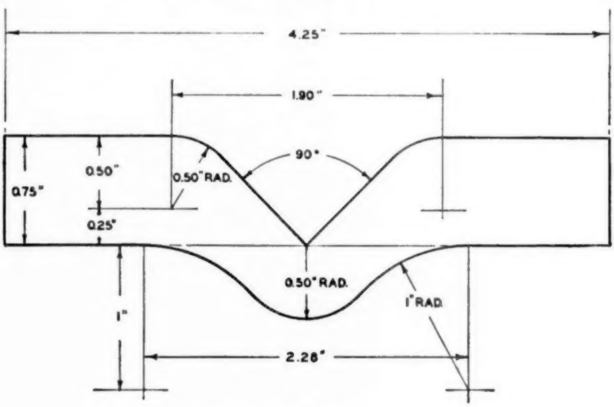

FIG. 4.—Angle specimen.

EXTENT OF TESTS

Graves[4] limited his statistical study to four stocks, tested only the A.S.T.M. type B crescent specimen in comparison with his angle specimen, and tested only 5 specimens—all with the grain—in arriving at each published coefficient of variation. The present authors have conducted tear tests on 14 stocks,

using the angle specimen and both A.S.T.M. type A and type B specimens, and have tested not less than 32 specimens of each shape from each stock (16 across grain and 16 along grain). The dies used in this statistical study and the specimens cut therewith are illustrated in Figure 1. The dimensions of the specimens are given in Figures 2, 3, and 4. The stocks tested are formulated in Table I and their tensile properties are listed in Table II. Natural rubber and seven synthetic rubbers were used in the preparation of these various stocks.

DETAILED PROCEDURE

The stocks were taken off a mill or calender at 0.1-inch thickness and molded into sheets 9 × 12 inches, with a nominal thickness of 0.08 inch. The direction of the grain, if any, was arranged to be in the longer dimension of the sheet. From each of four sheets of every stock excepting stocks 2, 3, and 4, four specimens were cut parallel to the grain direction and four specimens were cut at right angles to the grain direction with each of the three dies shown in Figure 1. Specimens were prepared in this manner from eight sheets of each of stocks 2, 3, and 4. Thus for each die, not less than 16 specimens of every stock were tested across grain and not less than 16 specimens were tested along grain.

The apparatus manufactured by the Akron Equipment Company was used

Table I

Composition of Stocks Tested

Stock No.	1 Hevea gasket	2 GR-S gasket	3 GR-S gasket	4 Perbunan-26 gasket	5 Perbunan-26 gasket	6 Perbunan-26 hose	7 Perbunan-26 hose
Smoked sheet	100.0	—	—	—	—	—	—
GR-S	—	100.0	100.0	—	—	—	—
Perbunan-26	—	—	—	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Micronex Standard (MPC)	—	—	—	—	—	50.0	—
Statex-B (FF)	—	50.0	50.0	70.0	60.0	—	—
Pelletex (SRF)	—	—	—	—	—	40.0	80.0
Thermax (MT)	—	—	—	—	—	—	40.0
Stearic acid	1.0	—	—	1.0	1.0	1.0	1.0
Heliozone	3.0	3.0	3.0	3.0	3.0	2.0	—
Cottonseed oil	2.5	—	—	—	—	—	—
Naftolen 510	—	—	20.0	—	—	—	—
Cumar P-10	—	—	—	—	—	10.0	—
Piccocizer-30	—	—	—	—	—	10.0	—
Bardol	—	—	—	—	—	10.0	—
Dibutyl phthalate	—	8.0	—	—	—	—	—
Dibenzyl sebacate	—	8.0	—	—	—	—	—
Tributoxyethyl phosphate	—	8.0	—	10.0	15.0	—	10.0
Plasticizer-SC	—	—	—	10.0	15.0	—	10.0
Age-Rite Resin D	1.0	—	—	—	—	—	—
Neozone-A	—	—	—	—	—	1.0	—
Captax	0.5	—	—	2.0	2.0	—	—
Altax	0.5	—	—	—	—	—	1.75
Tuads	0.5	—	—	3.0	3.0	—	—
Thionex	—	2.0	2.0	—	—	0.3	—
Diphenylguanidine	—	—	0.4	—	—	—	—
Sulfur	0.75	0.4	0.6	—	—	1.2	1.75
Selenium	—	—	—	0.1	0.1	—	—
Cure (min. at ° F)	20/290	25/310	20/310	20/310	25/310	40/300	60/280

TABLE I—*Continued*

Stock No.	8 Hycar OR-15 gasket	9 Neoprene-FR gasket	10 GR-M gasket	11 GR-M hose	12 GR-M hose	13 Thiokol-ST hose	14 Thiokol-FA hose
Hycar OR-15	100.0	—	—	—	—	—	—
Neoprene-FR	—	100.0	—	—	—	—	—
GR-M	—	—	100.0	100.0	100.0	—	—
Thiokol-ST	—	—	—	—	—	90.0	—
Thiokol-LP-2	—	—	—	—	—	10.0	—
Thiokol-FA	—	—	—	—	—	—	110.0
Zinc oxide	5.0	—	10.0	5.0	5.0	—	10.0
Litharge	—	10.0	20.0	—	—	—	—
Magnesia-XLC	—	—	—	4.0	4.0	—	—
Micronex Standard (MPC)	—	—	—	—	30.0	—	—
Statex-B (FF)	—	50.0	—	—	—	60.0	—
Pelletex (SRF)	50.0	—	—	—	—	—	60.0
Thermax (MT)	—	—	20.0	125.0	30.0	—	—
Stearic acid	1.0	0.5	1.0	1.0	2.0	0.5	0.5
Circo LP oil	—	30.0	10.0	10.0	10.0	—	—
Petrolatum	—	—	—	—	3.0	—	—
Paraffin	—	—	2.0	1.0	—	—	—
Pine tar	10.0	—	—	—	—	—	—
Dibutyl phthalate	—	—	—	—	—	—	—
Brown substitute	—	—	10.0	—	—	—	—
Neozone-A	1.0	2.0	2.0	2.0	2.0	—	—
Altax	1.75	—	—	—	—	—	0.3
Diphenylguanidine	—	—	—	—	—	—	0.1
G.M.F.	—	—	—	—	—	1.5	—
Sulfur	1.75	1.0	—	—	—	—	—
Cure (min. at ° F)	60/274	50/310	80/310	40/287	30/300	60/260	40/300

for cutting the nick in the A.S.T.M. specimens. The razor blades in this apparatus were set at 0.02-inch extension beyond the bearing surface of their respective holders.

The thickness of the specimens at the point of tear was measured with a micrometer gage. The tear tests were performed on the Scott L-6 machine. The A.S.T.M. type A specimen was held in vice-jaw clamps; the A.S.T.M. type B specimen and the angle specimen were held in self-tightening clamps. All tear tests and the tensile tests previously mentioned were conducted at 82° ± 5° F.

TABLE II

TENSILE PROPERTIES

Stock No.	Rubber	Application	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Modulus at 200% elongation (lbs. per sq. in.)
1	Hevea	Gasket	2920	790	40
2	GR-S	Gasket	1410	700	140
3	GR-S	Gasket	1790	680	230
4	Perbunan-26	Gasket	2310	590	440
5	Perbunan-26	Gasket	2170	700	250
6	Perbunan-26	Hose	2080	580	1080
7	Perbunan-26	Hose	2010	280	1650
8	Hycar OR-15	Gasket	1840	750	270
9	Neoprene-FR	Gasket	1490	330	570
10	GR-M	Gasket	1800	880	110
11	GR-M	Hose	1720	350	1090
12	GR-M	Hose	2610	380	1330
13	Thiokol-ST	Hose	1020	160	—
14	Thiokol-FA	Hose	1420	360	860

RESULTS

The results of the tests were calculated as the force in pounds per inch thickness required to tear the specimen. The individual results are not given here because of their voluminosity, but the arithmetic means of the results are given in Table III. The data in Table III show that the tear resistance

TABLE III

ARITHMETIC MEAN OF TEAR RESISTANCE VALUES, POUNDS PER INCH THICKNESS

		Type A specimens			Type B specimens			Angle specimens		
Stock No.	Rubber	Across grain	Along grain	Diff.	Across grain	Along grain	Diff.	Across grain	Along grain	Diff.
1	Hevea	198	197	+1	149	147	+2	104	101	+3
2	GR-S	230	234	−4	227	216	+11	148	139	+9
3	GR-S	235	222	+13	221	214	+7	168	166	+2
4	Perbunan-26	297	299	−2	251	253	−2	215	205	+10
5	Perbunan-26	316	312	+4	225	223	+2	186	181	+5
6	Perbunan-26	379	363	+16	338	341	−3	236	225	+11
7	Perbunan-26	183	197	−14	187	203	−16	153	160	−7
8	Hycar OR-15	212	216	−4	179	179	0	159	150	+9
9	Neoprene-FR	87	93	−6	74	89	−15	93	92	+1
10	GR-M	158	155	+3	121	115	+6	101	101	0
11	GR-M	356	270	+86	361	257	+104	238	203	+35
12	GR-M	273	327	−54	266	313	−47	216	212	+4
13	Thiokol-ST	233	266	−33	232	241	−9	183	230	−47
14	Thiokol-FA	271	263	+8	272	281	−9	290	303	−13

values obtained with the angle specimen were slightly less influenced by grain than the tear resistance values obtained with the A.S.T.M. specimens. These data also show that the A.S.T.M. type A specimen generally gave values which were greatest in magnitude, followed in turn by the A.S.T.M. type B specimen and the angle specimen. There seemed to be no correlation between the values obtained by the three methods; consequently the procedure using the angle specimen should not be employed as a replacement for an A.S.T.M. procedure in any case requiring a reliance on previously accumulated tear resistance data.

A study of the tear resistance data in Table III in comparison with the tensile data in Table II leads to the conclusion that there was no correlation between tear resistance as determined by any of the three methods on the one hand and tensile strength, ultimate elongation, or modulus on the other hand. An outstanding example of lack of correlation was Stock 13. Even though this stock had a tensile strength of only 1020 pounds per square inch and an ultimate elongation of only 160 per cent, its tear resistance by any of the three methods was far superior to the corresponding tear resistances of Stocks 1, 9, and 10, which had much better tensile properties.

PRECISION OF TESTS

The criterion used for comparing the precision of the three methods was the coefficient of variation. The coefficient of variation is the standard deviation of a set of values divided by the arithmetic mean of the set and expressed as a percentage. The standard deviation is the root mean square of the individual deviations from the arithmetic mean.

The coefficients of variation calculated from the tear resistance values obtained with each of three types of specimens are given in Table IV. These

TABLE IV

COEFFICIENT OF VARIATION OF TEAR RESISTANCE VALUES

Stock No.	Rubber	Type A specimens		Type B specimens		Angle specimens	
		Across grain	Along grain	Across grain	Along grain	Across grain	Along grain
1	Hevea	4.9	4.5	8.7	4.1	2.7	2.7
2	GR-S	7.7	13.4	8.5	10.9	4.4	6.1
3	GR-S	10.2	11.1	10.3	11.2	6.3	5.0
4	Perbunan-26	10.3	8.7	6.3	6.8	4.9	4.0
5	Perbunan-26	13.8	11.7	5.8	7.1	4.3	5.4
6	Perbunan-26	9.0	7.0	10.7	7.4	1.6	4.7
7	Perbunan-26	5.6	7.5	6.0	7.2	8.0	4.5
8	Hycar OR-15	6.2	7.3	4.9	5.3	4.3	3.1
9	Neoprene-FR	10.9	7.4	8.8	6.9	6.4	10.8
10	GR-M	12.5	13.7	7.7	7.1	3.5	3.3
11	GR-M	6.7	6.3	9.9	6.8	6.0	1.7
12	GR-M	13.1	7.7	15.2	19.0	3.9	4.6
13	Thiokol-ST	8.9	11.5	19.2	12.5	15.5	12.9
14	Thiokol-FA	7.9	8.8	10.3	9.3	12.2	11.5
	Arithmetic mean	9.1	9.0	9.5	8.7	6.0	5.7
	Median	9.0	8.2	8.8	7.2	4.7	4.7

coefficients show that the precision of the test using the angle specimen was consistently better than the precision of the other tests except in the cases of Stock 7 across grain, Stock 9 along grain, Stock 13 both directions, and Stock 14 both directions. The arithemetic means and the medians of the coefficients determined in each direction with each specimen show a distinct superiority for the angle specimen. The medians of the coefficients are perhaps the better basis for this comparison because the anomalous values obtained with Stocks 13 and 14 have less influence on the medians than they do on the arithmetic means.

Buist and Kennedy[5] pointed out that testing with the angle specimen gives an indication of the force to initiate a tear, whereas testing with the crescent specimen determines the force to continue tearing. From this standpoint the test using the angle specimen seems to be more important, since a tear must be started before it can be continued. This fact, together with the greater precision of the test using the angle specimen, are strong arguments for its adoption in lieu of the present A.S.T.M. tear tests.

In conclusion, it should be emphasized that only one angle-die was used in this study. It could well be that the variation introduced into the test by using more than one angle-die would decrease the precision of this test below that of the test with the crescent specimens. The use of more than one die in the case of the latter specimens would probably not affect the precision, since it is the nick in the crescent specimens which is the critical factor.

ADDENDUM

Since the completion of these tests the authors have been advised by Graves[6] that the angle specimen used in this work is not the same as the angle specimen originally designed[4]. The angle specimen used by the authors was copied after the drawing given in Graves' paper. Several critical dimensions were missing from this drawing, so that it was necessary to scale the dimensions directly from the drawing. The original angle specimen as employed by Graves is shown in Figure 5. It will be noted that the points of difference

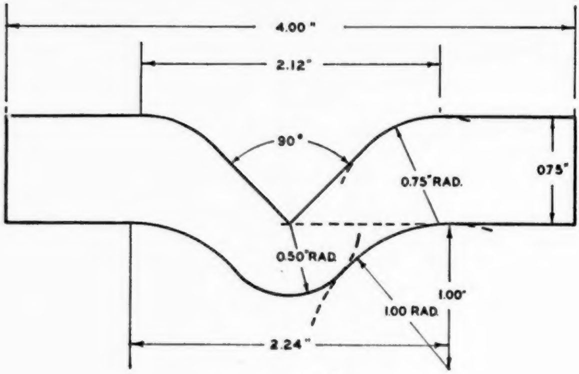

FIG. 5.—Angle specimen designed by Graves.

between this specimen and the specimen used by the authors are the length and the outside radius at the 45° bend.

The authors believe that their angle test-specimen gives essentially the same results as the true Graves specimen, since the small difference in length has no effect on the results, and the difference in radius would be expected to have a negligible effect. This statement is not made with the intention that the authors' angle specimen shall be adopted in lieu of the true Graves specimen, but merely to justify the application of the conclusions of this work to the true Graves specimen.

REFERENCES

[1] Am. Soc. Testing Materials, Method D624-44.
[2] Poules, *India Rubber World* **103**, 41 (Feb. 1941).
[3] Buist, *Trans. Inst. Rubber Ind.* **20**, 155 (1945); RUBBER CHEM. TECH. **18**, 486 (1945).
[4] Graves, *India Rubber World* **111**, 305 (1944); RUBBER CHEM. TECH. **18**, 414 (1945).
[5] Buist and Kennedy, *India-Rubber J.* **110**, 809 (1946).
[6] Graves, F. L., private communication.

CORRELATION OF LABORATORY AND SERVICE ABRASION TESTS OF RUBBER TIRE TREADS *

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Laboratory abrasion tests are run for control, development, and research purposes in most rubber laboratories. The question "How well do the results of a particular abrasion test correlate with performance in a particular service application?" is constantly being asked. It was the assignment of the authors of this report to obtain data and opinions on this question from representative rubber technologists.

PROCEDURE AND RESULTS

A questionnaire was submitted to a number of laboratories which the section members felt were most representative of the laboratories interested in abrasion testing and which would be most likely to have data on the correlation of laboratory and field tests. The questions asked were the following:

1. What type of laboratory abrasion tests do you use?
2. What type stocks are tested on the various machines used?
3. What degree of correlation do you find between laboratory and field tests?
4. Do you follow the A.S.T.M. Standards Methods D 394 and, if not, in what respects do your methods deviate?

Method D 394 at the present writing includes three methods for determining abrasion resistance[1]. These are the Du Pont or Williams method, the National Bureau of Standards method, and the U. S. Rubber Co. method.

Other machines which were mentioned in answers to the questionnaire included the Goodyear Angle Abrader described by Vogt[2], the Lambourn (British Dunlop) machine described by Lambourn[3], and the Goodrich machine not yet described in any publication. In the latter method the sample, in the form of a sheet approximately 0.1 inch thick, is cemented to the periphery of a pneumatic tire, of small diameter, inflated to a fixed air pressure. The wheel on which the tire is mounted is driven against a drum on which the abrasive is mounted. The drum is also driven, but at a fixed differential in surface speed to that of the tire. A controlled stream of dust is allowed to drop on the

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abrasive for the purpose of preventing its gumming. This method incorporates two features which are departures from the methods previously used. These are the pneumatic cushion and the use of dust to prevent gumming of the abrasive.

The results obtained are given in Tables I to III and Figures 1 to 5. In addition to data obtained in answer to the questionnaire, additional published data are shown in Figures 6, 7, and 8.

TABLE I

TIRES

Laboratory	Methods used	Degree of correlation with road	A.S.T.M. methods used
No. 1	Du Pont	Unsatisfactory—see Figure 1	Essentially
No. 2	Du Pont	Fair after aging test buttons—see Figure 2	Essentially
	Goodrich	Fairly good for natural rubber—see Figure 3	
No. 3	Goodyear Angle (modified)	Fair with limitations*—see Figure 4	
No. 4	Goodyear Angle (modified)	Fair with limitation†	
No. 5	None		
No. 6	Goodyear Angle	Not reported	
	Du Pont	Fair to poor—see Figure 5	Essentially
	U. S. Rubber	Not reported	Essentially
	Lambourn	Fair, with results in about the same order as given by the Du Pont machine	
No. 7	Goodyear Angle	Good with limitations‡	
No. 8	U. S. Rubber	Good to poor§	Some deviation

* For comparison of different carbon blacks the correlation is very good. Laboratory tests tend to magnify differences found in service tests. Factory-mixed and tubed stocks should be used rather than laboratory-mixed stocks for best results. Softener variations including fat acid cannot be successfully compared. Pigments loading variations must be kept within a narrow range. Compounds of widely different compositions cannot be compared.

† Correlation is good if the following precautions are observed: (1) a minimum of eight wheels should be tested per compound; (2) tests should be run both before and after oven aging, particularly when GR-S is being tested; (3) an equilibrium running temperature should be attained before a test is started; (4) a standard should be run with each group of experimental wheels; (5) the test wheels should be systematically alternated on the different machine mounts, and (6) a minimum of 3 to 4 cc. should be abraded from the sample.

‡ Carbon-black variations give good correlation between laboratory and road tests. Fat acid variations do not. This test is less sensitive to modulus or hardness variations than other methods.

§ High fat acid content introduces an appreciable error. Correlation for GR-S compounds poorer than for natural rubber.

TABLE II

HEELS AND SOLES

Laboratory	Laboratory method used	Degree of correlation	A.S.T.M. method followed
No. 1	Bureau of Standards	Fairly good	Yes
No. 2	Bureau of Standards	Fair	Essentially
No. 3	Du Pont	Doubtful*	Essentially—2½ garnet paper used
No. 4	Bureau of Standards	Fair†	Yes
No. 5	Bureau of Standards	Fair with limitations‡	Yes
No. 6	Bureau of Standards	Fair with limitations§	Essentially

* For best correlation the compounds tested must be in the same hardness range, have approximately the same state of cure, and contain the same amount and type of softeners.

† Correlation is not very accurate. It is better for natural rubber than for GR-S.

‡ When minor compounding variations are tested the correlation is fair. When widely different types of compounds are tested it is poor.

§ Fair for materials of similar composition only. Plastics or high resin stocks give false results.

The conclusions reached after consideration of the answers to the questionnaire are as follows.

1. Reliable data were available only with respect to tire treads. Data and opinions on other products were few and conflicting.

2. There was general agreement that the correlation between laboratory tests and performance of rubber tire treads was fair for most of the abrasion

TABLE III

MISCELLANEOUS

Laboratory	Laboratory method used	Products	Degree of correlation	A.S.T.M. method followed
No. 1	Du Pont	No specific product	No data	Essentially
No. 2	Du Pont	Belt covers—chute linings	No data	Essentially
	Wyzenbeck	Elastic plastics	Thought to be fair	
No. 3	Du Pont	Hose and belt covers	Doubtful	Yes
		Chute and tank linings*	Doubtful	
No. 4	Du Pont	No specific product	No data	Essentially

* Satisfactory for distinguishing good from poor compounds and for control purposes. It does not distinguish small differences. Because of the wide variety of conditions to which these products are subjected in service, precise correlation would not be expected.

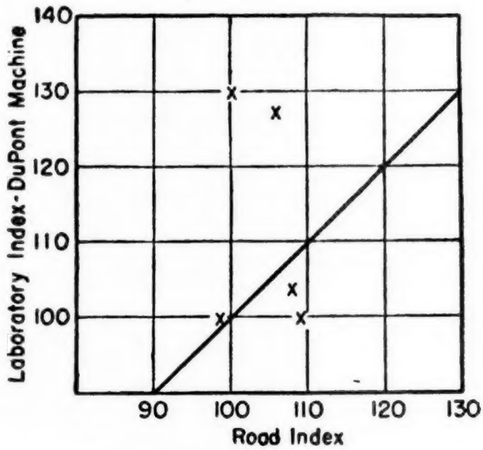

FIG. 1.—Correlation of laboratory and road tests. Data from laboratory no. 1.

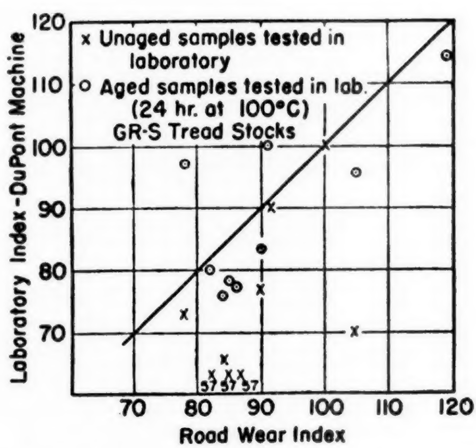

FIG. 2.—Correlation of laboratory and road tests. Data from laboratory no. 2.

testing machines in use, but the correlation was satisfactory in each case for only a limited range of compounding variations.

(*a*) Correlation is not good if the compounding variations include variations in fat acid or softener.

(*b*) Correlation is not good when various base polymers are compared. Several reports indicated that the correlation was less satisfactory for GR-S than for natural rubber.

(*c*) Correlation is not good when radically different compounding techniques are compared.

(*d*) Correlation is not generally good when various grades of carbon blacks are compared.

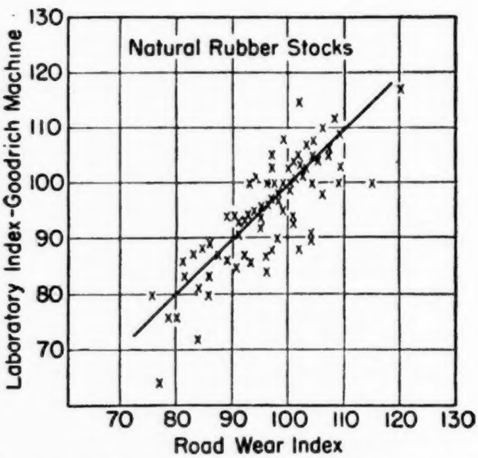

Fig. 3.—Correlation of laboratory and road tests. Data from laboratory no. 2.

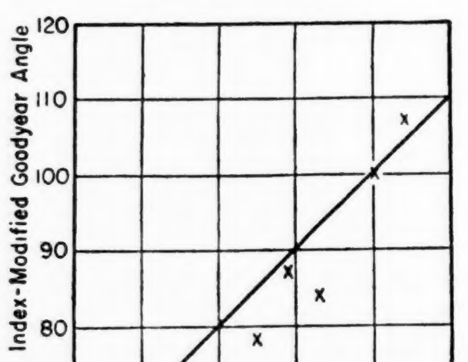

Fig. 4.—Correlation of laboratory and road tests. Data from laboratory no. 3.

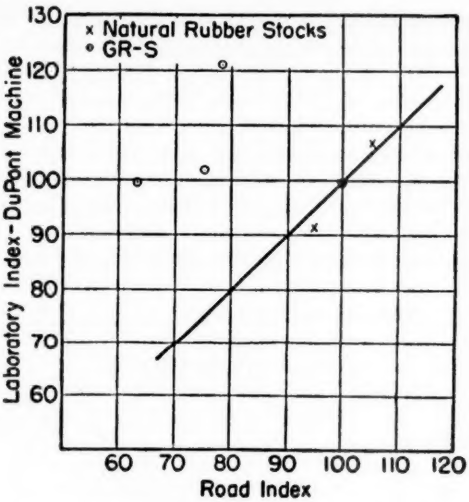

FIG. 5.—Correlation of laboratory and road tests. Data from laboratory no. 6.

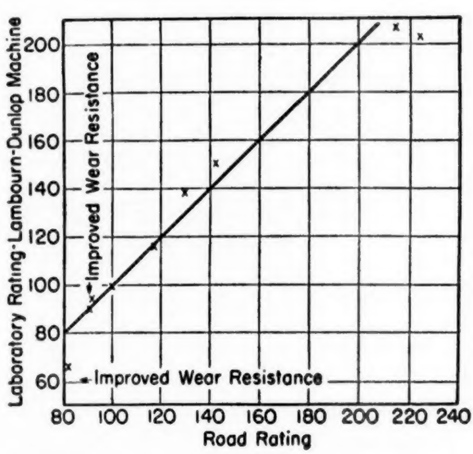

FIG. 6.—Correlation of laboratory and road tests. Data from Lambourn. (*I.R.I.*, Vol. 4, pp. 210–234, 1928–1929.)

3. The Du Pont machine is the most popular of those used for tire-tread work. The Goodyear angle abrader is the next most popular. In the footwear industry the Bureau of Standards Abrader is most widely used.

The reasons for failure of correlation are important since they indicate in what respects present laboratory methods are inadequate. The following possible reasons for disagreement on tire treads have been deduced from the comments received from various laboratories and from the personal experience of the members of this section:

1. Different road tests do not necessarily rate two different compounds in the same order. This may occur if the two tests are run under different condi-

tions, as, for example, if the tire designs are different, if the average temperature during the road tests is different, or if the abrasive character of the road surfaces is different. Thus, if road tests do not invariably rate a series of compounds in the same order, a precise correlation between laboratory tests and all road performance tests is not possible.

2. The state of cure is usually not the same in the laboratory test specimen and in the tire tread. If there were a constant difference this would not be as objectionable, but the probabilities are that it is variable.

3. If the laboratory test-specimens are made from stock mixed on a laboratory mill, the degree of pigment dispersion and the amount of breakdown of the

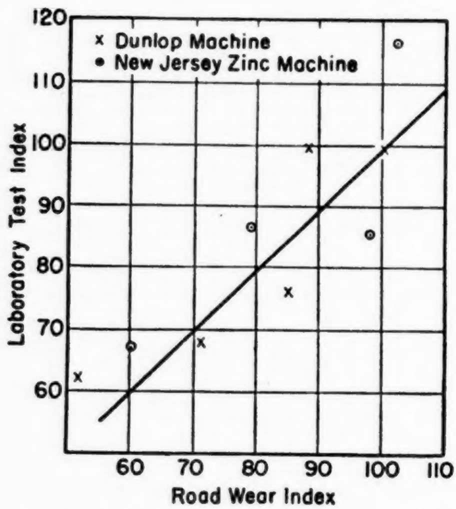

FIG. 7.—Correlation of laboratory and road tests. Data from report of Subcommittee XIV, *India Rubber World*, Vol. 81, No. 2, Nov. 1, 1929.

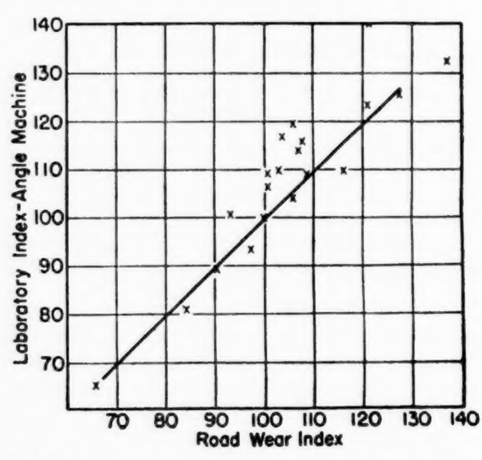

FIG. 8.—Correlation of laboratory and road tests. Data of J. L. Tronson and A. W. Carpenter, "Abrasion Tests of Vulcanized Rubber Compounds Using an Angle Abrasion Machine". *Proceedings*, Am. Soc. Testing Mats., Vol. 31, Part II, p. 908, 1931.

rubber are likely to be appreciably different from the factory mixed stock used on the tire.

4. The rate of wear changes in the course of a tire test due to the stiffening or softening resulting from continued cure or aging. This factor may at times be responsible for reversing the relative position of two stocks. This does not occur in laboratory tests, at least to the extent that it does in service.

5. Laboratory tests are usually made to proceed too fast. The nature of the abraded surface and the particles removed indicate a somewhat different process than occurs on the road.

6. The temperature coefficient of abrasive wear is high and is different for different stocks and different polymers. Laboratory tests may and probably do rate the various stocks at a different temperature level from road tests.

7. The abrasion of a tire tread is intermittent, a particular point on the tread contacts the road only once in each revolution. Many of the laboratory tests are continuous.

8. Laboratory tests tend to over-emphasize the effect of high modulus. This is probably associated with the difference in cushioning of the test-specimen, that is, a pneumatic cushion in the tire and only the deflection of a relatively thin block of rubber in the laboratory test. (The Goodyear angle abrader is somewhat better in this respect than the Du Pont machine and the Goodrich method eliminates it by the use of a pneumatic cushion.)

9. Laboratory tests are frequently erratic as a result of the abrasive becoming filled up or rendered gummy by the character of the stock being tested. This does not occur on the road, primarily for the reason that the abrasive track is being constantly renewed.

Many of these points were brought out in the discussion following the Symposium on Abrasion Testing of Rubber[4]. Specifically, the difficulty of duplicating road ratings from time to time, the temperature effect, the exaggeration of the modulus effect in most laboratory tests, and the problem of gumming of the abrasive track were discussed.

One of the most consistent objections to results from laboratory tests is that of gumming the abrasive. Because of this constantly recurring complaint it would be desirable if some attention could be given to eliminating this difficulty, either by the method of dusting or by using a continuously renewed track. Other methods, such as the suggestion that the samples be extracted before testing, might be considered.

There appears to be no immediate necessity for revising the methods as they now appear in A.S.T.M. Standard D 394. This is based on the results of the questionnaire, which showed that the present methods are followed with but minor deviations.

Because of the popularity and generally good experience with the Goodyear angle abrader, some consideration should be given to including this method in Standard D 394.

SUMMARY

There appears to have been no substantial improvement in the degree of correlation between laboratory abrasion tests and service tests on rubber tires since the 1931 Symposium on Abrasion Testing of Rubber[4]. The limitations with respect to compounding variations are essentially the same today as then.

The data on rubber products other than tires are too few to permit any conclusion to be drawn.

The reasons for the failure of laboratory tests to correlate with road results are many and varied. Some of these are listed in this report. They represent not only weaknesses in the laboratory procedures but also difficulties in standardizing service tests.

A better laboratory test method should incorporate the following features:

1. Cushion the test-specimen to minimize the modulus effect.
2. Provide means to prevent gumming of the abrasive.
3. Provide means to conduct the test over a range of temperatures.
4. Slow the rate of wear, partly by abrading intermittently and partly by use of less load and duller abrasive.
5. Use a test-specimen of a size which can be cut from a tire tread if desirable.

REFERENCES

[1] 1946 Book of A.S.T.M. Standards, Part III-B, p. 282.
[2] Vogt, *Ind. Eng. Chem.* **20**, 208 (1928).
[3] Lambourn, *Trans. Inst. Rubber Ind.* **4**, 210 (1928).
[4] *Proc. Am. Soc. Testing Materials* **31**, II, 895 (1931).

THE BRABENDER PLASTOGRAPH IN THE RUBBER LABORATORY *

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One of the most important operations in the rubber industry is the preliminary softening of crude rubbers by mastication or other means before the mixing operation. Better tools for the laboratory investigation of this operation are of great interest.

The Brabender plastograph is an instrument designed primarily for the study of materials less viscous than ordinary rubber. Behre and Gohde[1] reported on its use for the evaluation of pigments in rubber, but instead of rubber being used as the vehicle, a less viscous hydrocarbon was used. One of these instruments has been modified slightly for handling rubber and has demonstrated interesting possibilities for the study, on a small scale, of the mastication operation.

APPARATUS AND PROCEDURE

The apparatus, as modified, is illustrated in Figures 1 and 2. It consists of a jacketed mixing chamber with a pair of rotors which rotate in opposite directions, one at 90 r.p.m. and the other at 60 r.p.m. The rotors are driven by a $\frac{1}{3}$ h.p. motor through an integral reduction unit and a gear box. The motor shell is mounted on bearings, and by means of a series of levers the reaction of the motor shell to the load required to turn the rotors in the mixing chamber actuates a scale and a recorder. Adjustable weights on one end of the lever

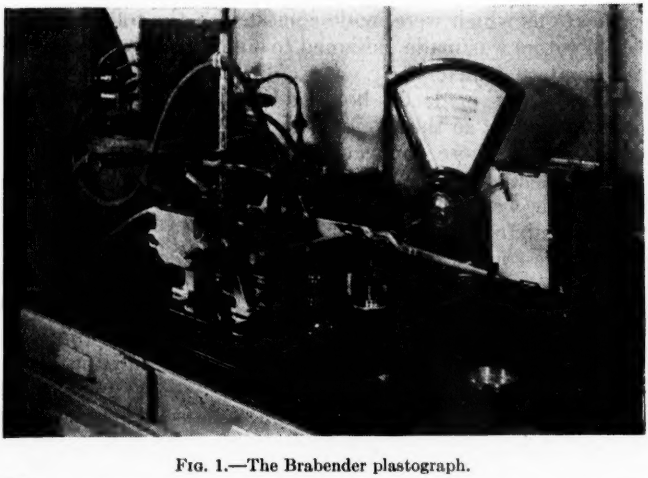

Fig. 1.—The Brabender plastograph.

* Reprinted from the *India Rubber World, Natural and Synthetic,* Vol. 117, No. 1, pages 62–64, 74, October 1947. This paper was presented before the Division of Rubber Chemistry at its semiannual meeting, Cleveland, Ohio, May 26–28, 1947.

arm make possible adjustment to zero when operating empty, and a weight pan on the other end permits adjustments to maintain the recorder pen within the chart range when tough or soft materials are being handled. For the GR-S reference rubber X-289, a 1,500-gram weight was required. A reduction or an increase of 500 grams on the pan changes the chart reading by 240 units. The scale and chart units are arbitrary. The lever mechanism has several adjustments to accommodate materials of varying consistencies. For rubber, the least sensitive adjustment is used. Also a dash pot is mounted on the lever arm, and may be adjusted to minimize wild fluctuations of the recorder arm.

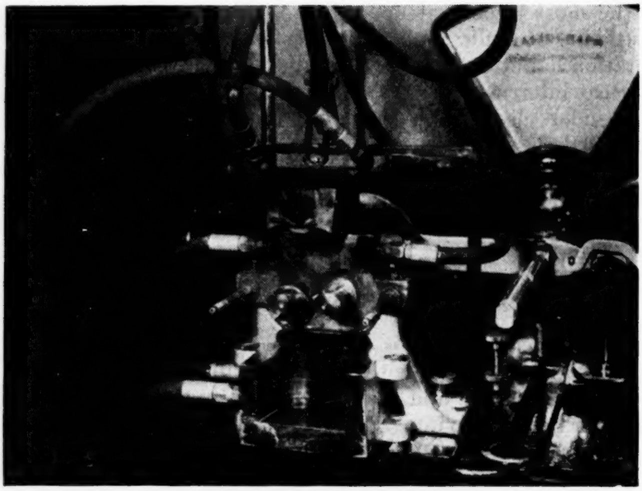

FIG. 2.—Close-up of Brabender plastograph mixing chamber.

The modifications which were made consisted of the following.

A new set of rotors was made, designed to simulate the action of rotors used in conventional internal mixers.

A jacketed ram was made for holding the material in the mixing space, with a lever arrangement so that weights could be used to hold the ram down.

A set of substantial hose connections was installed suitable for handling ethylene glycol at temperatures up to 160° C.

Improved glands were installed on the rotor shafts to prevent leakage of material from the mixing chamber.

The temperature-control device supplied with the equipment was replaced by a DeKotinsky regulator in series with a latch-in relay.

The capacity of the mixing chamber is between 60 and 70 cubic centimeters. For masticating experiments, batches of 60 grams (natural rubber and GR-S) were used. Smaller batches do not adequately fill the mixing chamber, and larger batches are not so effectively masticated.

The temperature at which a test was run, unless otherwise mentioned, is reported as the temperature of the fluid circulated through the jacket of the mixing chamber. The temperature of the rubber is not necessarily the same, since at low fluid temperatures heat is generated during the mastication, and the rubber temperature is thus higher than the jacket temperature, while at

the highest temperatures some heat is lost, and the rubber temperature is slightly below the jacket temperature. Measurements with the fluid at 24° C showed a rise in temperature of 35° C after GR-S was masticated 15 minutes. With the fluid temperature at 150° C, the rubber temperature was found to be 146° C.

In running a test, the bath temperature is first regulated to the desired level, and at this temperature the weights on the lever arm are adjusted to give a scale reading of zero with the motor running.

The charge of rubber is placed in the mixing chamber, the ram lowered and the recording chart started. Weights may be added to the pan at this point if it is known that such an adjustment is necessary to keep the recorder within its range. The test is then run for the desired time interval, which may be as short as 5 minutes or as long as 60 minutes, depending on the information desired.

RESULTS

Figure 3 shows a typical curve obtained by using 60 grams of GR-S, with the jacket maintained at 150° C. During the first five minutes of mastication the chart shows wide fluctuations in the consistency. This condition is due

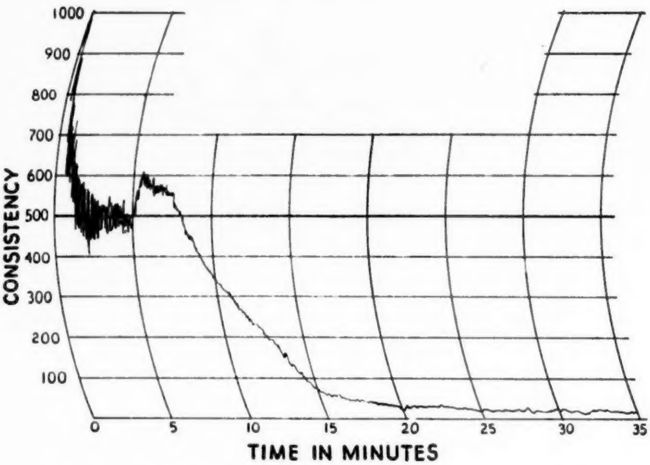

Fig. 3.—Consistency-time curve—GR-S (X-289) masticated at 150° C.

to the alternate sticking and slippage of the rubber past the rotor and the housing. This type of behavior in larger internal mixers has been discussed by Allen and Schoenfeld[2]. During this period the rubber is softening (as will be shown below), but the consistency reading shown by the chart is not a true measure of its value. At the point at which these fluctuations cease, the rubber adheres to the rotor, at least sufficiently to damp almost completely these fluctuations. Beyond this point the rubber shows a fairly constant rate of softening for about seven or eight minutes, after which the rate decreases to zero in from five to ten minutes more. The measurements which we have used to characterize the breakdown properties of a rubber in this test are: the time to reach the point at which the pen fluctuations cease (referred to hereafter as the time for adhesion to occur), the rate of change of consistency

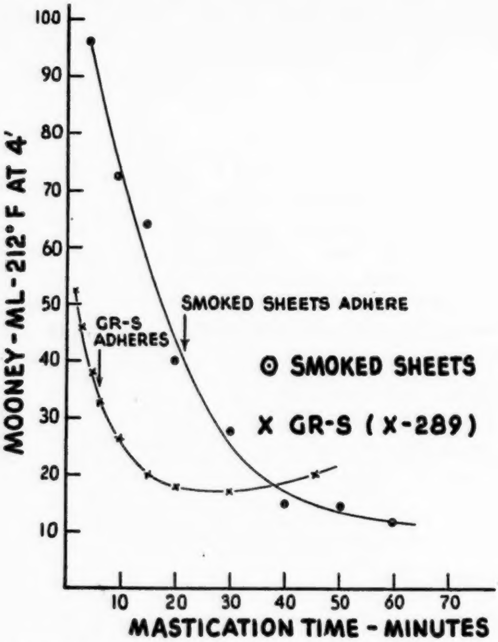

FIG. 4.—Mooney plasticity *vs.* mastication time in the plastograph at 150° C for smoked sheet and GR-S (X-289).

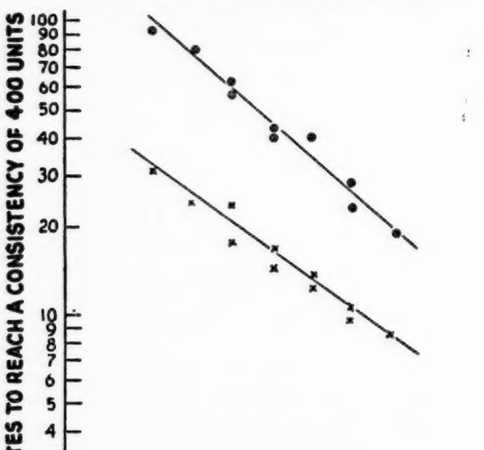

FIG. 5.—Time required to reach a specific consistency *vs.* temperature for smoked sheet and GR-S (X-289).

immediately beyond this point, or the total time required to reach a specific value of consistency.

Figure 4 shows Mooney plasticity values for both natural rubber (No. 1 ribbed smoked sheet) and GR-S (X-289 reference rubber) after various intervals of mastication at 150° C in the plastograph. This illustrates the point mentioned above that softening occurs during the interval before adhesion to the rotors takes place. This time is indicated on the curves. The rate of softening before and after this point is not appreciably different for either natural rubber or GR-S.

Figure 5 shows the effect of mastication on both natural rubber and GR-S over a range of temperatures. In this curve the log of the time required to reach a consistency of 400 on the scale (with the pan weights used) is plotted against the rubber temperature. Based on these results, the temperature coefficient[3] of the softening rate for natural rubber is 1.47 and for GR-S 1.36.

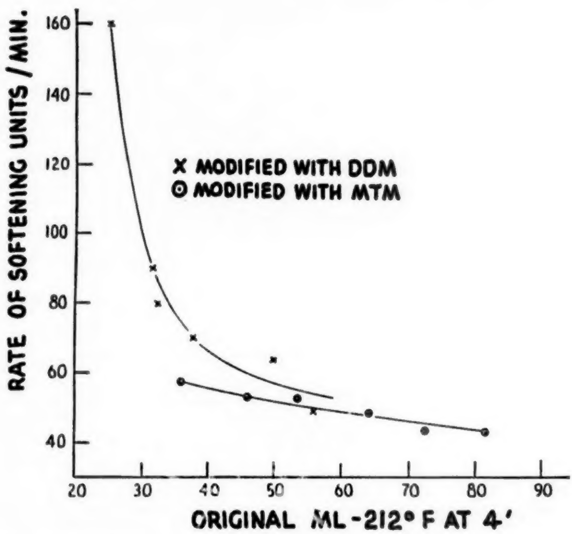

FIG. 6.—Original Mooney plasticity *vs.* rate of softening for rubber with different modifiers.

It was observed that modifications of GR-S made with a lower Mooney plasticity gave a higher rate of softening when masticated in the plastograph at 150° C. To study this further, two series of polymers were prepared in the laboratory with varying concentrations of modifiers, but in each case with conversions carried to 72 ± 0.5 per cent. One modifier was dodecanethiol (DDM), and the other a blend of mixed tertiary thiols (MTM) (60% C_{12}, 20% C_{14}, 20% C_{16}).

The results are illustrated in Figure 6. The two sets of rubbers showed similar rates of softening at 55 ML and above, but quite different results below this point. In the lower plasticity ranges, the MTM modified rubbers soften at a lower rate than the DDM-modified rubbers. This difference was confirmed on factory-scale processing tests. To process the MTM-modified rubbers satisfactorily, it was necessary to prepare them at a lower original Mooney plasticity so that, with the lower rate of softening during mastication,

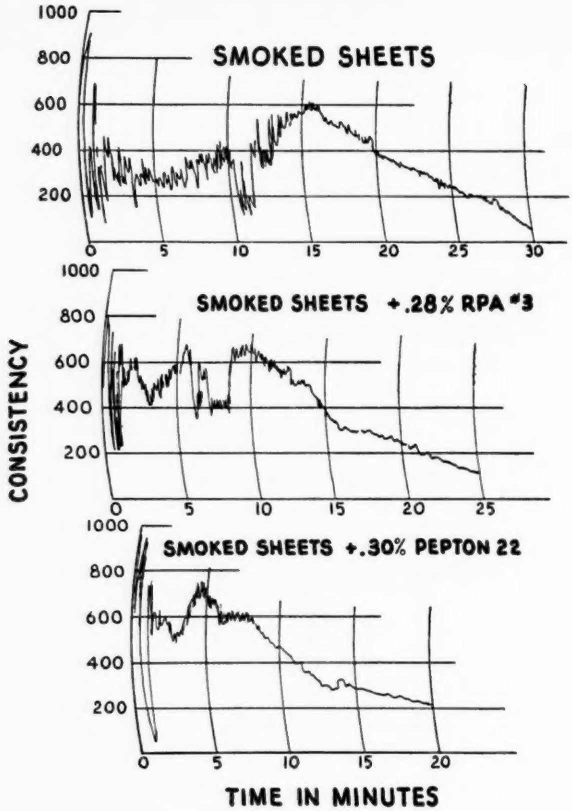

FIG. 7.—Consistency-time curves—masticated at 150° C.

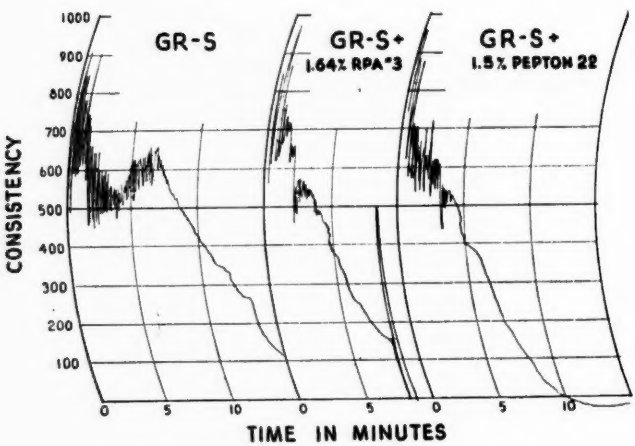

FIG. 8.—Consistency-time curves—masticated at 150° C.

they would arrive at approximately the same consistency as the DDM-modified rubbers in the same processing time.

One of the uses to which this instrument can be put is in the study of chemical plasticizers or peptizers. As an illustration, natural rubber, GR-S, and GR-I were masticated at 150° C, with and without the commercial peptizing agents RPA No. 3 (xylenethiol active agent) and Peptone-22 (*0,0'*-dibenzamidodiphenyl disulfide). The effects produced are shown in Figures 7, 8, and 9 and in Table 1. Both materials are seen to be effective peptizers for all three rubbers.

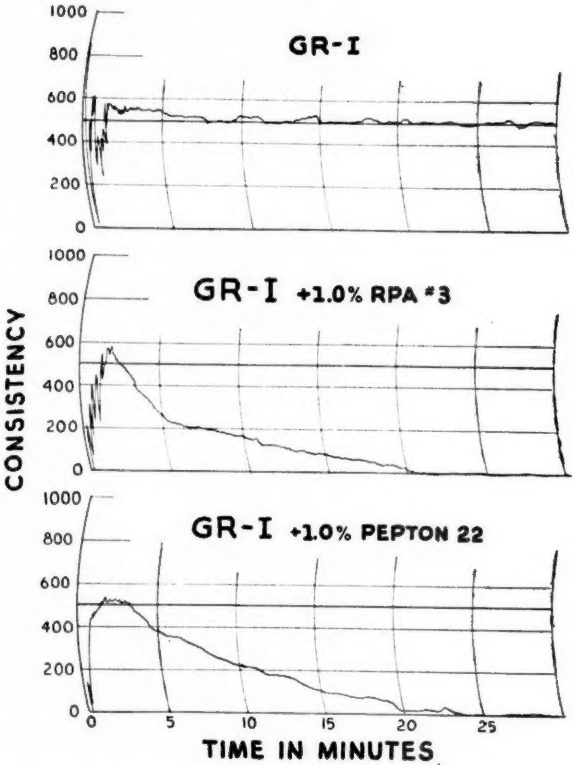

FIG. 9.—Consistency-time curves—masticated at 150° C.

TABLE 1

	Time required to reach a consistency of 400 (minutes)
Smoked sheet	$20\frac{1}{2}$
+0.28% RPA No. 3	$14\frac{1}{2}$
+0.39% Peptone-22	11
GR-S (X-289)	10
+1.64% RPA No. 3	$4\frac{3}{4}$
+1.50% Peptone-22	5
GR-I	>30
+1.0% RPA No. 3	$3\frac{3}{4}$
+1.0% Peptone-22	$4\frac{3}{4}$

The reproducibility of the test is quite satisfactory. The GR-S standard reference rubber X-289 was run at 150° C a total of 20 times over a period of six months, with the following results:

	Time for adhesion (min.)	Rate of softening (units/min.)	Time required to reach a consistency of 400 (min.)
Average	5.6	59.3	10.2
Standard deviation	.63	5.1	.71

CONCLUSIONS

With suitable modifications the Brabender plastograph can be used to advantage in studying, on a small scale, the factors which influence the changes in consistency of rubbers during their mastication.

Typical results reported herein show that the temperature coefficient of the rate of breakdown for natural rubber is 1.47 and for GR-S, 1.36.

The rate of softening of butadiene-styrene copolymers is shown to depend, among other factors, on the original consistency of the rubber and the type of modifier used in polymerization.

The influence of commercial peptizing agents on the rate of softening of natural rubber, GR-S, and GR-I at 150° C is shown.

The reproducibility of the mastication test was found to be good.

REFERENCES

[1] Behre and Gohde, *Kautschuk* **15**, 160 (1939).
[2] Allen and Schoenfeld, *Ind. Eng. Chem.* **25**, 1102 (1933).
[3] The ratio of the time of mastication at one temperature to that at a temperature 10° C higher.

SPONTANEOUS COAGULATION OF HEVEA LATEX *

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Introduction.—Fresh Hevea latex can only be kept fluid for a few hours. After tapping in the morning, one observes a thickening of the latex in the afternoon, and in the evening the whole mass is coagulated. This coagulation may begin sooner or later, depending on circumstances. Contamination with rain water running along the bark of the tree may cause the latex to spoil during collection.

Several investigators have tackled the problem, but no theory has been able to account fully for the facts observed.

The most obvious explanation that coagulation occurs as a result of acidification cannot hold, as the acidity does not drop below pH 6.0–6.3, an observation which has been made by several authors[1].

Even if the pH is held constantly at 7.0 by adding continuously small amounts of sodium hydroxide, spontaneous coagulation is not prevented or retarded. It is obvious that in the hours after tapping several changes take place in the latex.

Spoon[2] showed that the potential acidity, *i.e.*, the amount of alkali needed to neutralize the latex, increases.

Ultee and van Dillen[3] proved the formation of carbon dioxide. Schrieke[4] made extensive experiments on this subject, and reached the conclusion that carbon dioxide leads to an increase of the potential acidity but that the spontaneous coagulation is not affected by it.

Soap coagulation of latex.—The present concept of spontaneous coagulation is based on an entirely new method of coagulating latex, *viz.*, by means of soaps.

A few years ago the author[5] found that fresh Hevea latex coagulated on the addition of sodium salts of fat acids or sulfonic acids. Many salts of the same type have been investigated, most of which prove to be usable.

The coagulating power is restricted to a certain concentration range (Figure 1). There is a limit on the lower side and one on the higher side.

It is curious that the breadth of this range depends on the magnesium and calcium contents of the latex. Latex which has been freed from these ions by dialysis does not show any soap coagulation. On addition of magnesium or calcium salts to the dialyzed latex, soap coagulation is again possible. The dialysis of fresh latex is not possible, for partial coagulation occurs during dialysis. However, if the latex is first made alkaline with ammonia, dialysis continues to the end, and excess ammonia is removed at the same time.

The explanation of this kind of coagulation is that when soap is added to latex, the fat-acid ions are strongly adsorbed on the rubber particles, with resultant displacement of part of the protein molecules. In this way the colloid chemical nature of the rubber particles is changed. From protein-stabilized particles they are transformed into soap-stabilized particles.

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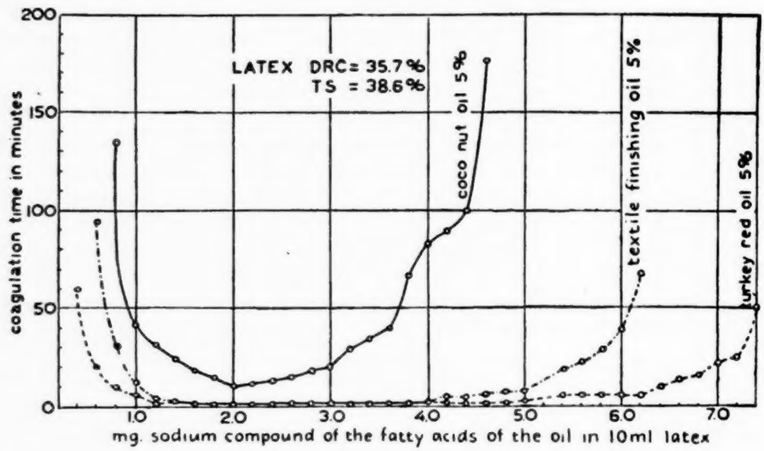
However, these soap-stabilized particles are not stable in a liquid containing Mg^{++} or Ca^{++} ions, and thus are coagulated. Only if the soap concentration is such that they predominate does the latex remain stable.

Spontaneous coagulation explained as "soap-coagulation."—Similarly, it was found that spontaneous coagulation depends on the Mg^{++} and Ca^{++} contents of the latex. Latex freed from these ions by dialysis does not coagulate spontaneously, and can be kept fluid for days. It is true that this is not the way to preserve latex; for after a few days putrefaction sets in, causing the development of obnoxious gases and partial coagulation of the rubber. However, these phenomena are outside the scope of this discussion.



In actual practice it is not even necessary to dialyze the latex. The addition of a small amount of ammonia, *e.g.*, 1 g. NH_3, is sufficient to precipitate the Mg^{++} ions in the form of magnesium-ammonium phosphate. The Ca^{++} ions apparently are of little importance. Putrefaction of the latex may be prevented by the addition of a preservative, such as sodium pentachlorophenate.

Spontaneous formation of soap ions in the latex.—One thing remains to be explained. How is it possible that, during the storage of latex, soap ions are formed? Altman[6], in this laboratory, has made extensive analyses of the organic components of Hevea latex. He found that 1 liter of latex contains about 10 grams of ether-soluble components, consisting of glycerides (45 per cent) and lipoids (55 per cent). Before spontaneous coagulation sets in, there is a steady saponification of these components, fat-acid ions are formed, and these combined with the magnesium and calcium salts already present in the latex. The cause of saponification is not yet clear, and the whole mechanism is rather complicated.

In strong support of the author's theory is the following experiment, which shows that if the saponification is accelerated artificially by the addition of fat-splitting enzyme, spontaneous coagulation is promoted.

Pancreas lipase was prepared according to Willstätter[7] from the pancreas glands of a cow. A very active extract in glycerol was obtained. Samples of fresh field latex were mixed with different amounts of lipase solution, shortly after arrival at the laboratory. To avoid any other factors which might in-

fluence spontaneous coagulation, mixtures were made of active enzyme solutions with different amounts of the same solution inactivated by heating at boiling temperature for half an hour. Any slight precipitate was filtered off. The results are given in Table 1.

TABLE 1

ACCELERATION OF SPONTANEOUS COAGULATION BY LIPASE

Cc. of lipase solution Active	Inactivated	Cc. of latex	Time of coagulation
0	15	30	more than 7 hours
2	13	30	230 minutes
4	11	30	160 minutes
6	9	30	115 minutes
8	7	30	100 minutes
10	5	30	90 minutes
12	3	30	77 minutes
14	1	30	65 minutes
15	0	30	55 minutes

The pH of the latex-enzyme mixtures was 6.1, measured with a glass electrode.

The addition of small amounts of ammonia does not affect the spontaneous coagulation. Larger amounts are harmful because Mg ions are precipitated. This is illustrated in the following table.

TABLE 2

INFLUENCE OF AMMONIA ON THE ENZYME ACCELERATED COAGULATION

Cc. of active lipase solution	Cc. of 2 *N* ammonia	Cc. of latex	pH	Coagulation after
15	0.1	30	6.1	60 minutes
15	0.5	30	6.8	70 minutes
15	1.0	30	7.7	12 hours
15	2.0	30	8.6	more than 12 hours

Conclusions.—The spontaneous coagulation of Hevea latex cannot be attributed entirely to the formation of acidic substances.

The chief mechanism is the following. As soon as the latex has left the tree the lipoids and glycerides form fat-acid ions, which combine with the magnesium and calcium salts already present, and lead to coagulation of the latex.

REFERENCES

1 Hauser and Scholz, *Kautschuk* **1927**, p. 304; van Harpen, *Arch. Rubbercultuur* **15**, 1 (1931); Paton, *Chem. & Ind.* **58**, 246 (1939); Stamberger, *Nature* **143**, 520 (1939); *India Rubber World* **35**, 103 (1940).

2 Spoon, *Arch. Rubbercultuur* **3**, 313 (1919).

3 Ultée and Dillon, *Arch. Rubbercultuur* **6**, 18 (1922).

4 Schrieke, *Arch. Rubbercultuur* **24**, 470 (1940).

5 Van Gils, *Arch. Rubbercultuur* **25**, 385 (1941).

6 Altman, *Arch. Rubbercultuur* **25**, 142 (1941).

7 Willstätter, referred to by Wolvenkamp and Griffioen, *Z. physiol. Chem.* **223**, 36 (1934).